BEHAVIOUR OF AROMATIC HYDROCARBONS IN URBAN ATMOSPHERES

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December 2000

A thesis submitted in partial fulfilment of the requirements of the University of Northumbria at Newcastle for the degree of Doctor of Philosophy

In Collaboration with the Division of Public Health and Environmental Protection, Newcastle City Council

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ACKNOWLEDGEMENTS

Firstly, I would like to thank Dr. John Newham, for his support and physical chemistry knowledge over the last five years, and Dr. Bill Tomlinson, for his statistical assistance.

I would also like to thank the Environment Team of Newcastle City Council for their logistical and instrumental support, and I would like to acknowledge their generous financial assistance throughout the research period. In particular, I would like to offer my greatest thanks to Mr. Edwin Foster, for his selfless support over the last five years, and his approachability and encouragement throughout.

A big thanks goes to the technical staff at the University of Northumbria, particularly David Osborne and Dave Wealleans, who always seemed to have the answers I needed. Many thanks to Jim Creigton for the assistance with EDXRF and thermal methods.

Last, but by no means least, a huge thank you to my family and friends, particularly my sister for her humour, Pauline for her unconditional support throughout the last two years, and Mik, Miller, Neil, Mike, Louise, Stu, Paul, Johnny, and Peter, for making the last five years of my life, through lows and highs, likely to be the best I will ever have.

ABSTRACT

Quasi-continuous measurement of benzene, toluene, ethylbenzene and isomers of xylene in northern England has been performed using an automated thermal desorption - gas chromatography - flame ionisation detector (TD-GC-FID) system. The TD-GC-FID system was mounted in a mobile laboratory, together with a TEOM (Tapered Element Oscillating Microbalance) system for particulate monitoring, and a weather station.

Both systems have been applied to urban and suburban sites in order to examine the behaviour of BTEX aromatics at these localities, under a range of boundary layer environments. Measurement of BTEX aromatics and particulate matter has also been performed within a bus depot, a site which was effectively isolated from the free boundary layer overnight, to contrast the behaviour of BTEX in sunlit and non-sunlit atmospheres.

Time series analysis of the concentration ratios of individual BTEX aromatics has been performed and diurnal seasonality has been demonstrated at a number of sites. Significant differential removal of individual BTEX aromatics has been found to occur overnight. Relative removal rates have been measured for this period, and values indicate that accepted tropospheric transformation mechanisms of the BTEX aromatics are not responsible.

The available experimental and theoretical evidence collected in this research serves to support the supposition that a physical process, which is related to atmospheric temperature, volatility of individual BTEX aromatics, and pressures of individual BTEX aromatics, governs nocturnal differentiation of the concentration of BTEX aromatics.

A postulated effect, which may contribute to nocturnal differential, is preferential absorption of particular BTEX aromatics to a liquid organic carbon phase, which has been shown to be associated with diesel carbonaceous combustion aerosol. The latter supposition has been partially corroborated by the findings of a separate study exploring the composition of carbonaceous combustion aerosol by GCMS, XRF, DTA, DSC, and FTIR.

GLOSSARY OF TERMS

Aerodynamic Diameter	The aerodynamic diameter of a particle is the diameter which the particle would have if it were to be spherical in shape, to be of unit mass, and to have the same sedimentation rate
ASE	Accelerated Solvent Extraction
AUN	Automatic Urban Network
BC	Black Carbon
Boundary Layer	The part of the troposphere that is directly influenced by the presence of the earth's surface, and responds to surface forcing's with a time scale of about an hour or less.
BTEX	Benzene, Toluene, Ethylbenzene, and para-, meta- and orthoXylene
CCA	Carbonaceous Combustion Aerosol
Coarse Particle	Particles within the coarse particle mode, of between approximately 2.5μm to 10μm aerodynamic diameter
DETR	Department of the Environment, Transport and the Regions
DOAS	Differential Optical Absorption Spectroscopy
EC	Elemental Carbon
Fine Particle	Particles of between approximately 0.05μm and 2μm aerodynamic diameter
LOC	Liquid Organic Carbon
ML	Mobile Laboratory
NAEI	National Atmospheric Emissions Inventory
NAQS	National Air Quality Strategy (see Appendix 1).

NETCEN	National Environmental Technology Centre
NMVOC	Non-Methane Volatile Organic Compound
$NO_3^{\cdot}$	Nitrate radical
OC	Organic Carbon
$^{\cdot}OH$	Hydroxyl radical
PHEP	The Division of Public Health and Environmental Protection, Newcastle City Council
PM_{10}	Particulate Matter with an aerodynamic diameter of 10μm or less (or more strictly, particles which pass through a size selective inlet with a 50% efficiency cut-off at 2.5μm aerodynamic diameter)
ppb	Parts Per Billion (unless stated otherwise, by volume)
ppm	Parts Per Million (unless stated otherwise, by volume)
POCP	Photochemical Ozone Creating Potential
QUARG	Quality of Urban Air Review Group
RSD	Relative Standard Deviation
SACP	Surface Area Coverage Potential
SOC	Solid Organic Carbon
Solar Irradiance	Solar Irradiance describes the radiant energy emitted by the sun, over all wavelengths, that falls on the earth's surface each second on 1 square meter area (watt $metre^{-1}$)
SPME	Solid Phase Micro Extraction
TD-GC-FID	Thermal Desorption-Gas Chromatography-Flame Ionisation Detector
TEOM	Tapered Element Oscillating Microbalance
Troposphere	Layer of the atmosphere extending upwards from the earth's surface for about 10km

Ultrafine Particle	Particles typically between 1-10nm aerodynamic diameter

UNITS AND NOTATIONS

B	Benzene
[BTEX]	Concentration of individual BTEX aromatics e.g. daily mean [BTEX] implies the mean concentration of benzene, toluene, ethylbenzene and the isomers of xylene
$\bar{c}$	Mean molecular speed
d_a	Aerodynamic diameter
D_{BA}^{Y}	Diffusion coefficient of compound B in medium A (cm^2s^{-1}), at temperature Y (K)
d_e	Equivalent diameter (of a suspended particle)
EB	Ethylbenzene
F_a	Rate of mass transfer (or 'flux')
J	Reaction rate
J_0	Initial reaction rate
K	Temperature in units of Kelvin
K_H	Henry's Law constant
K_r	Restoring force constant
k_x^y	Reaction rate constant with species X, at temperature Y (^{e} signifies 298K)
MX	Metaxylene
OX	Orthoxylene
P_{VAP}	Vapour pressure of a pure substance
PX	Paraxylene
r	Correlation coefficient
r_e	Equivalent radius
Sigma [XY], Σ[XY]	The sum of the concentrations of X and Y

T_B	Boiling point of a pure substance at 1 atmosphere
T_M	Melting point of a pure substance
Tol	Toluene
$\Delta_f H^{\ominus}$	Enthalpy of formation at standard temperature and pressure ($kJ\ mol^{-1}$)
$\Delta H^{\ominus}_{VAP}$	Enthalpy of vaporisation ($kJ\ mol^{-1}$) at standard temperature and pressure
Σ[BTEX]	Sum of the concentrations of BTEX
ΣPMX	Sum of the concentrations of para and metaxylene
$\alpha_{[BTEX]}$	Proportion of individual BTEX aromatics over Σ[BTEX]
αX_B	Concentration gradient of B at the hypothetical plane ($mol\ cm^{-2}$)
μ	Viscosity of medium ($dyne\ s^{-1}\ cm^{-2}$)
σ, Stdev, SD	Standard deviation
[X]	The concentration of species X
$\overline{X}$[X]	Mean concentration of X
Z	Collision frequency

1 INTRODUCTION

1.1 THE NEED FOR ATMOSPHERIC RESEARCH

Over the last two centuries, the anthropogenic emission of many trace gaseous and aerosol species, almost exclusively to the lower atmosphere, has resulted in the perturbation of delicate chemical cycles within both the troposphere and the stratosphere. Indeed, many chemical species are today present in the atmosphere at permanent, detectable concentrations, only as a result of man.

The advent of regional, national and global atmospheric concerns, such as tropospheric photochemical smog formation, stratospheric ozone depletion, and greenhouse gas augmented global warming, has instigated extensive atmospheric interdisciplinary research, particularly over the last few decades.

The chemistry of the lower troposphere, the boundary layer, comprises the theme of this research.

1.2 RESEARCH OUTLINE

This research focuses upon a group of volatile organic compounds (VOCs): benzene, toluene, ethylbenzene, and otho-, meta- and paraxylene (BTEX), which are important anthropogenic pollutants, particularly in urban areas, as we shall see in the following chapter.

The collection of more than 80,000 individual boundary layer measurements between 1995 and 1998 for this research has only been possible through its collaborative nature, between the University of Northumbria and the Division of Public Health and Environmental Protection (PHEP), of Newcastle City Council.

2 LITERATURE REVIEW

The following chapter presents a review of the current literature and data regarding the tropospheric sources, behaviour, and sinks of BTEX aromatics. Urban aerosol is also reviewed, as later chapters explore the role of suspended carbonaceous aerosol in the fate of aromatic hydrocarbons within particular environments.

The physical and chemical diversity of BTEX aromatics and suspended particulate matter warrants separate sections of this chapter for their narration. However, in order that the motives for this research are established, we shall begin with an introduction into the impacts currently understood to be associated with exposure of man and the natural environment to BTEX aromatics, their secondary products, and suspended particulate matter.

2.1 HEALTH EFFECTS

Historically, it took very little time to establish an association between atmospheric pollution and impacts upon human health and the quality of life. Today, air pollution is a socially lively chapter of modern environmental concerns, driven to the forefront of an ever-increasing body of issues due to the combination of regional, national and global impacts that anthropogenic emissions have been shown to exhibit.

2.1.1 Benzene

Historical studies have shown that long-term exposure to benzene in the workplace can induce certain types of leukaemia known collectively as the non-lymphocytic leukaemia's [Rinsky et al., 1987]. Observations from epidemiological studies, and more recently, carcinogenesis bioassays, have corroborated earlier findings [Vigliani, 1976; Infante, et al., 1977; Maltoni and Scarnato, 1979; Rinsky et al., 1987].

On the basis of these studies, it is currently acknowledged that there is a risk from exposure of the general public to benzene at part per billion (ppb) concentrations. Although the risk is believed to be extremely small, it is very poorly defined within available literature and UK Government publications [Expert Panel on Air Quality Standards, 1994]. It is also recognised that benzene plays a significant role in the formation of secondary pollutants (discussed below) [Atkinson, 2000].

2.1.2 Toluene, Ethylbenzene and Xylene

To date, studies have not established a specific risk to human health through exposure to trace concentrations of toluene, ethylbenzene and isomers xylene representative of UK urban and rural atmospheres [Quality of Urban Air Review Group, 1994]. At mixing ratios of parts per million (ppm) and above, however,

symptoms have been observed, and as such occupational exposure standards have been assigned accordingly [Health and Safety Executive, 2000].

2.1.3 Secondary Pollutants

Arguably of far greater significance is the exposure of the general public to secondary pollutants. Secondary pollutants, such as ozone, formaldehyde and peroxyacetyl nitrate (PAN), are formed when oxides of nitrogen (NO_x) are mixed with hydrocarbons, including BTEX aromatics, and then irradiated with UV radiation (described in Section 2.3) [Mohan et al., 1996]. Modelled data suggest that in cities with high traffic density, BTEX alone may be responsible for more than 30% of secondary pollutant formation [Le Bras et al., 1995].

A number of secondary photochemical pollutants have been shown to exhibit deleterious effects upon man's health. Ozone is commonly considered the most significant photochemical oxidation product, because of the high concentrations recorded globally during photochemical smog episodes within and downwind of urban centres [Volz et al., 1981].

2.1.3.1 Ozone

The effects of tropospheric ozone on lung function have been well documented [Burnett et al., 1997]. Long term exposure to concentrations of ozone of approximately 100 ppb has been shown to cause slight inflammation of the airways. At 120 ppb symptoms include nose and throat irritation and can lead to hypersensitivity towards allergens such as pollen [Burnett et al., 1997].

Although recent investigations have found that individuals with asthma are not more significantly affected than healthy individuals, epidemiological studies have demonstrated a clear relationship between hospital admissions and ambient ozone concentration [McDonnell, 1991; Burnett et al., 1997; Holgate and Ayres, 1998].

2.1.4 Particles

Due to the considerable compositional and physical diversity of particulate matter, it has historically been very difficult to carry out controlled exposure of volunteers and animals. Therefore almost all understanding of the effects of airborne particles upon health appears to have come from epidemiological studies and other indicators of ill-health of the general public [Quality of Urban Air Review Group, 1996].

Several studies have shown marked contrast between cities where concentrations of particulate matter contrast greatly, and have found relatively good positive correlation's between hospital admissions and particle concentration [Cuddihy, 1983; Fraser, 1986; Boffetta, 1989; Butler, 1993; Expert Panel on Air Quality Standards, 1995].

In addition, carbonaceous particles (aerosols which are formed by combustion processes such as diesel engines) are of particular concern because many organic compounds associated with such matter are known or suspected carcinogens [Degobert, 1992; Butler, 1993].

2.1.5 Regulatory Framework

Policy makers have not ignored these widely accepted relationships between tropospheric pollution and impacts upon human health. Global, European and national standards and objective standards exist for (amongst other pollutants) benzene, ozone and particles. Although discussion of the legislative criteria pertinent to tropospheric pollutants falls outside the scope of this Thesis, a brief review of current UK urban air quality standards and objective values is presented in Appendix 1.

2.2 SOURCES AND DISTRIBUTION OF TROPOSPHERIC BTEX AROMATICS

There are no known significant natural sources of BTEX [Field et al., 1992]. Anthropogenic sources mainly comprise two groups – industrial sources (BTEX and many other aromatic hydrocarbons are essential chemical intermediates) and more importantly, the refinement, transportation, delivery (marketing), and combustion of petrol and diesel fuel.

The eleventh annual report from the UK National Atmospheric Emissions Inventory (NAEI), produced as part of the Department of the Environment Transport and the Region's (DETR) Air Quality Research Programme by the National Environmental Technology Centre (NETCEN), comprehensively demonstrates the range and significance of sources of Non-Methane VOCs (NMVOC) in the UK. An extract of this data relating to BTEX aromatics is presented below in Table 2.1, for 1997.

Although Table 2.1 does indicate a wide range of BTEX sources, within UK cities almost all BTEX aromatics arise though exhaust emissions from petrol fuelled vehicles. Studies conducted in the UK, Canada, Germany, and the USA, have indicated contributions from petrol fuelled vehicles to the total BTEX emission within urban centres of between 76-90% [Tims, 1983; Singh et al., 1992; Hearn, 1992; Expert Panel on Air Quality Standards, 1994].

Table 2.1 UK Tropospheric Sources of BTEX (1997)

Source (in decreasing order of magnitude)	Petrol fuelled road transport	Solvent use	Production processes	Road transport (petrol evaporation)	Other transport and machinery (1)	Diesel fuelled road transport	Stationary combustion (2)	Stationary combustion (3)	Extraction and distr. Fossil fuels	Waste treatment and disposal	Stationary combustion (4)	Other transport and machinery (5)	Nature	**Total**
Benzene	21.29	<0.05	7.26	1.46	1.20	1.70	2.95	0.15	0.56	0.08	0.96	0.17	0.00	**38**
Toluene	54.98	51.59	4.29	8.33	2.28	0.67	1.36	0.23	0.58	0.31	0.38	0.08	0.00	**125**
Ethylbenzene	15.92	0.35	0.07	1.94	0.57	0.67	<0.05	0.39	0.07	0.23	0.19	0.05	0.00	**20**
Paraxylene	24.31	6.54	3.91	2.77	0.83	0.67	<0.05	0.00	0.00	<0.05	0.00	0.05	0.00	**39**
Metaxylene	24.31	6.56	<0.05	2.77	0.83	0.67	<0.05	1.34	0.18	<0.05	0.02	0.05	0.00	**37**
Orthoxylene	19.10	7.12	0.10	2.34	0.67	0.67	<0.05	0.30	0.06	<0.05	0.09	0.05	0.00	**30**
Xylenes (6)	<0.05	24.74	5.12	<0.05	<0.05	<0.05	<0.05	<0.05	0.00	0.34	0.00	<0.05	0.00	**30**
Total	**135.6**	**96.9**	**20.8**	**19.6**	**6.4**	**5.1**	**4.3**	**2.4**	**1.5**	**0.9**	**1.6**	**0.4**	**0.0**	**319**

(1) Off-road vehicles, including naval shipping and military aircraft
(2) Commercial & residential
(3) Energy production
(4) Combustion in industry
(5) Other transport includes shipping railways and civil aircraft (excludes international bunkers)
(6) Unspeciated mixtures of m-, o- and p-xylene

Remarks

Adapted from the National Atmospheric Emissions Inventory, 1997

All values in kilotons (or $x10^3$ kg).

This data is considered to be accurate to approximately ±50% [National Atmospheric Emissions Inventory, 1997]

2.2.1 BTEX in Automotive Fuels

2.2.1.1 Benzene

Benzene is not a fuel additive, but is formed during fuel manufacture, which involves either catalytic reforming or steam cracking. Most petrol fuel is formed though catalytic reforming, which typically leads to final benzene concentration in the fuel of ~1-2% (current EU limit is 5%). The concentration of benzene in UK petrol fuels (leaded and unleaded) is about 2% [Expert Panel on Air Quality Standards, 1994]. Diesel fuels, however, are formed by hydrocracking of the gas oil fraction of crude oil, and contain relatively insignificant amounts of benzene [United States Environmental Protection Agency, 1998].

Benzene is released by road traffic through evaporation of fuel from the carburettor, fuel tank, other engine components, and as a result of fuel combustion [United States Environmental Protection Agency, 1998]. In addition, studies have shown that pyrolysis of non-benzene aromatics can contribute to the total benzene exhaust emission, even where a catalytic converter is in place [Marshall, 1988].

2.2.1.2 Toluene, Ethylbenzene and Xylenes

Aromatic hydrocarbons, including toluene, ethylbenzene and isomers of xylene, are added to petrol to raise the octane rating, thereby suppressing engine knock, increasing power, and providing smoother running engines. The aggregated concentration of toluene, ethylbenzene and xylene in fuel varies from between 5 and 30 % [United States Environmental Protection Agency, 1994].

Toluene, ethylbenzene and xylene are present in automotive exhaust emissions as a result of unburned fuel, and can also be emitted to the atmosphere through evaporation from engine components and the fuel tank [Rainbow et al., 1996].

2.2.2 Tropospheric Distribution of Benzene and Toluene in Tyne and Wear

Near real-time measurements of benzene and toluene in Tyne and Wear have been collected by Newcastle City Council's Division of PHEP since 1994 using Differential Optical Absorption Spectroscopy (DOAS) at a number of rooftop locations within the city of Newcastle upon Tyne, and a number of outlying districts.

The technique (detailed in Appendix 2) has been shown to be effective for a number of inorganic gases [Platt and Perner, 1979; Killinger et al., 1983; Sigrist, 1994]. However, a study by Barrefors (1996) illustrates DOAS's unacceptable analytical performance for aromatic hydrocarbons at concentrations representative of urban atmospheres, findings which have been corroborated through DOAS measurements collected by PHEP in a study in Sunderland City Centre (this particular study is discussed in Chapter 6 in terms of other inorganic determinants).

For these reasons, historical DOAS measurements of benzene and toluene by PHEP have not been reviewed within this study. No other data or comprehensive studies concerning the distribution of benzene and toluene in the district of Tyne and Wear are known.

2.2.3 Distribution of Ethylbenzene and Xylene in Tyne and Wear

No published studies concerning the tropospheric distribution of ethylbenzene and xylene in the district of Tyne and Wear are known.

2.3 THE FATE OF TROPOSPHERIC BTEX

2.3.1 Introduction

The effective management of atmospheric pollution, both locally and globally, requires a knowledge of atmospheric emission sources and source strengths (of relative ease to estimate for most anthropogenic sources) and a knowledge of the factors dictating the atmospheric lifetimes of pollutant species.

This section discusses the current understanding of tropospheric sinks of BTEX.

2.3.2 Removal Mechanisms

The principal processes of removal and / or transformation of volatile organic compounds (VOCs) and Semi-Volatile Organic Compounds (SVOCs) in the troposphere are wet and dry deposition (removal) [Bidleman, 1988] and reaction with ·OH radicals, NO_3· radicals, and with O_3 (transformation) [Finalyson-Pitts and Pitts, 1988; Carlier and Mouvier, 1988]. These processes, which dictate the tropospheric lifetime (τ) of a VOC in the atmosphere, have been summarised by Atkinson (1994):

$$\frac{1}{\tau_{OVERALL}} = \frac{1}{\tau_{WET\ DEPOSITION}} + \frac{1}{\tau_{OH}} + \frac{1}{\tau_{O_3}} + \frac{1}{\tau_{NO_3}}$$

Where tropospheric lifetime is defined as (using ·OH transformation as an example):

$$\tau_{OH} = \frac{1}{k_{OH}*[\cdot OH]}$$

In addition to the processes included above, photolysis in the free troposphere may contribute significantly to the overall rate of removal of a number of organic species, such as aldehydes and ketones. However, BTEX aromatics are not readily photolysed by solar radiation reaching the troposphere, even at equatorial latitudes [Atkinson and Aschmann, 1994].

2.3.2.1 Removal by Deposition to the Earth's Surface

For the majority of tropospheric pollutants, the significance of deposition to, and uptake by, the Earth's surface is currently not well understood [Derwent, 1995]. These processes are summarised in Table 2.2.

Table 2.2 Physical Removal Mechanisms of Organic Gases

Deposition Name	Process Description	Influencing the lifetime of	Remarks
Dry deposition	Adsorption or absorption to atmospheric aerosol, and consequent fallout / washout of particulate matter	Mainly SVOCs [a]	Can be more significant than reaction with ·OH for many SVOCs – studies indicate this may be a sink for more volatile compounds e.g. BTEX [b]
Dry deposition; uptake by plant tissue	Reaction and/or adsorption onto ground surfaces (soils and minerals, vegetation, plants)	Pollution near ground	Thought to be a slow process for most VOCs: e.g. the lifetime of CH_4 through dry deposition to soil surfaces is about 160 years [a]. Not well understood for BTEX but may be significant for xylene and ethylbenzene [c].
Absorption, dry deposition	Uptake at water surfaces	Pollution near ground, readily water soluble	BTEX sparingly soluble, with low partial pressures. See section discussing wet deposition below.
Wet deposition, wash out	Uptake by precipitation	Mainly readily water soluble species [d] e.g. COOH [e, f, g]	BTEX sparingly soluble, with low partial pressures. See section discussing wet deposition below.
Wet deposition, rain out.	Uptake by cloud droplets	Mainly readily water soluble species [d, e, f]	Can lead to aqueous phase transformation of organic species. Precipitation phase chemistry of BTEX not well understood [c].

[a] Oehme, 1991 [b] Cachier, 1998 [c] Goss and Eisenreich, 1996
[d] Hales, 1986 [e] Atkinson, 1995 [f] Bridleman, 1988
[g] Eisenreich et al., 1981

Wet deposition – Precipitation Scavenging

For any gas in contact with a liquid, such as a droplet of rainwater, molecules of that gas will, to some degree, partition from the gas into the liquid until an equilibrium condition is established. The position of that equilibrium is dependent upon the

concentration of the gaseous species in question (expressed as a partial pressure), the concentration already dissolved into the liquid (expressed as a molar concentration), and a Henry's Law constant (analogous to an equilibrium constant):

$$K_H = \frac{\text{Concentration}_{(aq)}}{\text{Partial Pressure}_{(g)}}$$

The Henry's Law constant demonstrates a dependence upon temperature as follows:

$$K_H = K_H^{\theta} \times \exp\left(\frac{-\Delta_{sol}H}{R}\left(\frac{1}{T} - \frac{1}{T^{\theta}}\right)\right)$$

Where

$$\frac{-d\ln K_H}{d1/T} = \frac{-\Delta_{sol}H}{R}$$

k_H^{θ} = Henry's Law constant at 298.15K

A compilation of Henry's Law constants and temperature dependence values for BTEX aromatics are presented in Appendix 3. Although many authors acknowledge that the process of wet deposition of aromatic hydrocarbons is slow compared to their tropospheric transformation, very few published measurements of the gas-precipitation distribution of aromatic hydrocarbons during storm events exist [Ligocki et al., 1985; Atkinson, 1994].

A single study by Ligocki, although not comprehensive, presents simultaneous gas and aqueous (precipitation) phase BTEX concentrations collected over a number of one to five day sampling periods during February, March and April of 1984. Henry's Law constants for toluene, ethylbenzene and the xylene's, calculated from these measurements, are presented in Table 2.3 with literature values of K_H for pure water at a number of temperatures.

Table 2.3 Henry's Law Constant (K_H) for BTEX Aromatics

Henry's Law Constant K_H (mol dm^{-3} atm^{-1})	Benzene	Toluene	Ebenzene	ΣMeta+para Xylene	Orthoxylene
Derived from tropospheric distribution during storm events (at 281K mean) [a]	NM	0.93	1.08	1.32	1.52
Literature Value [b] (at 298K)	0.18 [c]	0.16 [d, e]	0.13 [c, f]	0.14 [c, g]	0.22 [f]
Derived Literature Value (at 281K) [h]	0.39	0.33	0.36	0.32	0.45
Derived Literature Value (at 274K) [h]	0.59	0.49	0.62	0.51	0.67

NM = Not Measured

[a] Ligocki et al., 1985 [b] Values from published K_H measurements (e.g. head-space or bubble column technique as explained by Betterton, 1992)

[c] Yaws and Yang, 1992 [d] Kolb et al., 1992 [e] Neilsen, 1994

[f] Bissonette, 1990 [g] Ashworth et al., 1988

[h] Derivation using the temperature dependence expression as described earlier. Published values of $\frac{-\Delta_{soln}H}{R}$ are presented in Appendix 3.

Given the number of limitations of Logocki's work, such as climatic variability during sampling periods, tropospheric measurements of K_H show reasonable agreement with those derived through controlled experiments.

Elementary translation of these values into a theoretical description of precipitation scavenging of BTEX during a storm event is possible, if a number of assumptions regarding precipitation and the boundary layer are accepted, i.e.:

- that steady state meteorological conditions exist during the storm event;
- that BTEX partial pressure changes (reduces) through wet deposition only; and
- that equilibrium between aqueous (precipitation) and gas phase BTEX is reached during the lifetime of rain droplets.

The latter assumption is reasonable when one considers the residence time of precipitation in the boundary layer [Seinfeld, 1986].

Numerical modelling of precipitation scavenging of BTEX aromatics during a storm event (5mm $hour^{-1}$, for 3 hours) indicates a reduction of BTEX concentrations (from an initial concentration of 10 ppb of each aromatic) by 4%. As BTEX typically demonstrate a range of proportionally constant pressures in the lower atmosphere, wet deposition is theoretically predicted to cause very slight differential removal of BTEX aromatics, the extent of which is dependant upon the mean pressure difference of each aromatic, and atmospheric temperature.

This process is explored experimentally in Chapter 5.

Gas-Particle Distribution

What is less understood is the role of suspended particulate matter in the removal of organic gases from the troposphere. The deposition process of gases differs considerably from deposition of particles and therefore the deposition rate of BTEX depends upon the distribution between gas and particles phases. This phenomenon is discussed in Chapter 6, following a review of suspended particulate matter in Section 2.4.

2.3.3 Transformation Mechanisms

2.3.3.1 Introduction - photochemical smog

Photochemical air pollution or 'photochemical smog' was first observed in Los Angeles in the late 1940's and early 1950's [Haagen-Smit et al., 1953]. Photochemical pollutants are formed through a complex chain reaction, which begins when VOCs are mixed with oxides of nitrogen (NO_x) and irradiated with ultraviolet radiation, at temperatures of above 290K [Lymen et al., 1982; Hendry and Kenley, 1990; Muschack, 1990; Cicciolo, 1993; Carter et al., 1995]. Mixing of these reagents occurs mainly by turbulence, and to a lesser extent diffusion, and energy is provided by solar radiation. In most UK urban environments VOCs and NO_x are provided principally by road vehicle exhaust emissions, and the entire system has been likened to an 'atmospheric reactor' [Ciciolli, 1993].

Reactions occurring in these photochemical 'reactors' involve many free radical species. The termination steps of such chain reactions lead to the formation of ozone, aldehydes, PAN, hydrogen peroxide, organic and inorganic acids, and fine particulate matter [Cicciolo, 1993]. Examples of known products of the atmospheric oxidation of organic matter are presented in Table 2.4.

Table 2.4 Known Tropospheric Oxidation Products

Oxygenated Intermediate Class	Examples
Free Radicals and Ozone	O_3, $\cdot OH$, HO_2, $NO_3^{\cdot}$, RO_2
Saturated Carbonyls	HCHO, CH_3CHO
Saturated Dicarbonyls	CHOCHO, CH_3,COCHO
Unsaturated Carbonyls	CH_2=$CHCOCH_3$, CH_2=CCH_3CHO
Peroxides	HOOH, CH_3OOH
Organic Acids	HCOOH, CH_3COOH
NO_x Compounds	NO_2, N_2O_5, HNO_3, $CH_3C(O)OONO_2$

Adopted from Edney (1996)

2.3.4 The Hydroxyl Radical

It is recognised today that the hydroxyl radical is one of the most important trace species in the troposphere, reacting with almost all organic gases, including BTEX, leading to their complete oxidation [Fishman and Kowalczyk, 1980; Atkinson, 1989; Altshuller, 1989; Cicciolo, 1993; Marston, 1996].

2.3.4.1 Hydroxyl Radical Formation in the Troposphere

The primary source of ·OH radicals in the troposphere is the photolysis of O_3 to produce O (^1D) (Figure 2.1) [Atkinson and Arey, 1994].

Figure 2.1 Formation of ·OH from O_3

$$O_3 + h\nu \xrightarrow{\lambda\ 315\text{-}1200\ nm} O(^3P) + O_2$$

$$O(^3P) + O_2 + M \longrightarrow O_3 + M$$

$$O_3 + h\nu \xrightarrow{\lambda<315nm} O(^1D) + O_2$$

$$O(^1D) + M \longrightarrow O(^3P) + M$$

(Where M is O_2 or N_2)

$$O(^1D) + H_2O \longrightarrow 2\ OH$$

$O(^1D)$, an exited species, has sufficient energy to react with water vapour to generate ·OH radicals, or can be deactivated and relaxes back to ground state $O(^3P)$.

Other significant sources of the hydroxyl radical are the reaction of $O(^1D)$ with CH_4. [Atkinson and Areay, 1994]. In polluted atmospheres, it is also believed that formaldehyde is an important source of ·OH radical [Hewitt and Harrison, 1985].

2.3.4.2 Hydroxyl Radical Concentration

Much research has been directed over the last few decades to accurately measure directly and indirectly hydroxyl radical concentration (denoted [·OH] hereafter) in the free troposphere, as well as develop and apply predictive modelling techniques. The tropospheric concentration of ·OH is dependant upon its rate of formation and reaction, which in turn depends upon an number of parameters such as the tropospheric concentration of gas phase H_2O (which itself linked to ambient temperature) [Altshuller, 1989]. Also important are the concentration and the rate of photolysis of ozone, which will vary considerably with solar zenith angle and atmospheric ozone column density [Logan et al., 1981].

A wide range of analytical techniques have been applied for [·OH] measurement, such as laser-induced fluorescence (LIF) [Aderson, 1971; Wang et al., 1976; Davis et al., 1982; Hard et al., 1986; Shirinzadeh, et al., 1987; Hofzumahaus et al., 1996], long-path absorption spectroscopy (LPA) [Hübler et al., 1976; Perner et al., 1987; Platt et al., 1988], and the oxidation of ^{14}CO to $^{14}CO_2$ by ·OH radicals [Campbell et al., 1986; Campbell et al., 1988]. Studies have determined steady state and varying peak [·OH] values of the order of 10^6-10^7 molecules cm^{-3} close to ground level, and diurnal measurements have shown that maximum concentration occur at noon. Annual seasonality has also been demonstrated, with maximum concentration experienced during summer months (in the Northern Hemisphere).

Table 2.5 presents values of [·OH] from a recent comprehensive study by Hofzumahaus and co-workers (1996), carried out at a latitude comparable to Northern England, and includes modelled data for wintertime concentrations at a similar latitude.

Table 2.5 Measured and Modelled Tropospheric [·OH]

Method	Location	Date	Altitude	[·OH] (10^6 molecules cm^{-3})	Reference
Laser Induced Fluorescence	54°N, Germany	August	Ground	0400-0600hrs **0.0-0.2** 0800-1000hrs **2.0-9.0** 1200-1400hrs **5.0-10.0** 1400-1600hrs **4.0-1.0** 1600-1800hrs **0.0-1.0** all values ± 0.06	Hofzumahaus et al., 1996
Relative rate (to 1,1,1-$Cl_3C_2H_4$)	Northern Hemisphere	Diurnally, seasonally, and annually averaged	Ground	1	Prinn et al., 1994;
2-D model [1]	45°N 60°N	Wintertime, daytime maximum Wintertime daytime maximum	Ground Ground	0.02 <0.02	Crutzen and Gidel, 1983

[1] Northern hemispheric average

Adopted from Altshuller, 1989; Georgii and Warneck, 1999; Atkinson, 2000.

The modelled and experimentally measured data above demonstrates that mean [·OH] undergoes significant seasonal variation in atmospheres of England. At the time of writing of this document, experimentally determined wintertime [·OH] at latitudes of 60°N or greater were not known. Modelled wintertime ·OH concentrations are very low, which suggests that other sink mechanisms may be more prominent in winter months.

The major sinks for ·OH in the troposphere are believed to be reaction with CH_4 (~70%) and CO (~30%). Only a very small fraction of ·OH is removed through reaction with other species, such as NO_2 and other hydrogen containing organic matter [Altshuller, 1989].

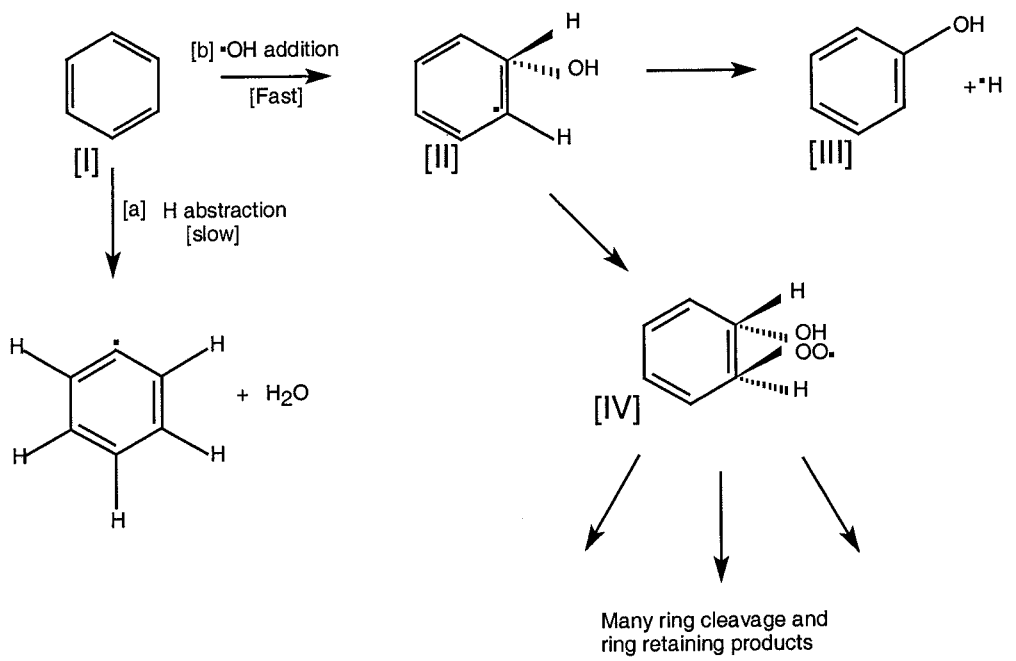
2.3.5 Reaction of BTEX with the Hydroxyl Radical

The ·OH initiated oxidation of BTEX aromatics is believed to be their major tropospheric sink [Knispel et al., 1990; Atkinson and Aschmann, 1994; Atkinson, 1994]. At the time of writing of this Thesis, an entire mechanistic description of the oxidation of BTEX was not complete [Atkinson, 2000].

The hydroxyl radical attack upon the BTEX aromatics is rate determining, after which, product radicals react very rapidly with other species (usually O_2) or decompose to their reactants [Atkinson and Arey, 1994].

Figure 2.2 mechanistically describes the primary oxidation step of benzene by ·OH radical.

Figure 2.2 ·OH Radical – Benzene Reaction Mechanism



The initial reaction step takes place via hydrogen abstraction [a], or preferentially, by ·OH addition to the benzene ring [b] [Tsan and Bozzelli, 1996; Hester and Harrison, 1995; Atkinson, 1994; Atkinson, 1989]. Under atmospheric conditions, the aromatic adduct [II] may undergo thermal decomposition (lifetime of the ·OH-toluene· adduct

before thermal decomposition is 0.2-0.3s at 298K [Knispel et al., 1990; Atkinson, 1994]) or may react predominately with molecular oxygen to form hydroxycyclohexadienylperoxy radicals [IV], although Le Bras (1995) and Atkinson (1995) claim that reaction with NO and NO_2 is possible, and reaction rate constants have been measured.

2.3.5.1 ·OH Radical Reaction Rate Values: the Primary Oxidation Step

Table 2.6 presents a compilation of measured and modelled reaction rate constants for ·OH and BTEX, the measurement of which has been discussed at length by Atkinson (1985, 2000), and Colbeck and Mackenzie (1993). The table demonstrates very good agreement between individual measurements of BTEX reaction rates. The data also indicates the broad ranging reactivity of BTEX aromatics with ·OH.

Table 2.6 Compilation of Rate Constants for ·OH-BTEX Tropospheric Reaction

Compound	Technique [1]	Temperature (inc. range of investigation) (T, K)	Rate constant, k_{OH} (x 10^{-12} cm^3 $molecules^{-1}$ s^{-1})	Reference
Benzene	Rrate (to OH + ethene) [2]	298 (250-1017)	1.24 ± 0.09	Tully et al., 1981
	LP-RF	298 ± 2 (244-870)	1.16 ± 0.25	Lorenz and Zellner, 1983
	RR-GC	292	1.2 (cm^3 s^{-1})	Kerr and McElroy, 1993
	DF-RF	292	1.0	Devolder, 1994
Toluene	FP-RF	298 (213-1046)	6.36 ± 0.6	Tully et al., 1981
	DF-RF	292	6.1	Kerr and McElroy, 1993
	DF-RF	292	6.0	Devolder, 1994
	RR-FTIR	292	6.6	Becker et al., 1993
Ethylbenzene	FP-RF	298	7.95 ± 0.50	Ravishankara et al., 1978
	LP-RF	298	7.1	Simpson, 1995

Table 2.6 Continued overleaf

Table 2.6 Continued				
O-xylene	Rrate (OH + ethene) [2]	300	14.0	Cox et al., 1980
	FP-RF	298 (298-970)	14.2 ± 1.7	Nicovich et al., 1981
	LP-RF	298	13.0	Simpson, 1995
M-xylene	FP-RF	298 (298-427)	24.0 ± 2.5	Perry et al., 1977
	FP-RF	298	25.4 ± 3.5	Nicovich et al., 1981
	FP-RF	298	24.8	Prinn et al., 1994
P-xylene	FP-RF	298.0 (298-428)	15.3 ± 1.7	Perry et al., 1977
	LP-RF	298	14.3	Simpson, 1995
	RR-GC	292	15.0	Becker et al., 1993

[1] Technique:

FP-RF	Flash Photolysis – Resonance Spectroscopy
DF-MS	Discharge Flow - Mass Spectrometry
LP-RF	Laser Photolysis – Resonance Spectroscopy
RR-FTIR	Relative Rate Technique – Fourier Transform IR Absorption
DF-RF	Discharge Flow – Resonance Spectroscopy.
Rrate	Relative Rate Technique
RR-GC	Relative Rate - Gas Chromatography
RR-FTIR	Relative Rate - Fourier Transform Infrared Spectroscopy

[2] $k_{[OH + ethene]} = 8.45 \times 10^{-12}$ cm^3 $molecules^{-1}$ s^{-1}

2.3.6 Reaction of BTEX with Other Species

Measured rates of reaction of the hydroxyl radical with BTEX indicate this to be their principal sink. For comparative purposes, Table 2.7 presents the lifetime of BTEX due to reaction with ·OH, and two other reactive tropospheric species, the nitrate radical (NO_3·) and ozone. Lifetimes have been calculated as described in Section 2.3.2.

Table 2.7 Tropospheric Lifetime of BTEX by Gas Phase Transformation Mechanisms

Compound	Reactive Species		
	$\cdot OH$[a]	$NO_3^{\cdot}$[b]	O_3[c]
Benzene	12 days	> 2½ years	> 5 years
Toluene	2½ days	1 year	> 5 years
Ethylbenzene	1 day	40 days	> 5 years
Orthoxylene	12 hours	60 days	> 5 years
Metaxylene	7 hours	100 days	> 5 years
Paraxylene	11 hours	50 days	> 5 years

[a] For 12hr daytime average $\cdot OH$ radical concentration of 1.6×10^6 molecules cm^{-3} [Prinn et al., 1994]

[b] For 12hr night-time average $NO_3^{\cdot}$ radical concentration of 5×10^8 molecules cm^{-3} [Atkinson, 1991]

[c] For 24hr average O_3 concentration of 7×10^{11} molecules cm^{-3} [Logan, 1985]

[Adapted from Lymen et al., 1982; Atkinson, 1989; Atkinson, 1991; Atkinson, 1994]

Table 2.7 demonstrates the dominant role of $\cdot OH$ in the tropospheric chemistry of the BTEX aromatics, and also demonstrates that the BTEX aromatics are virtually unreactive to ozone. The $NO_3^{\cdot}$ radical does play an important role in the fate of tropospheric BTEX aromatics, the significance of which is discussed below.

2.3.6.1 The Nitrate Radical, $NO_3^{\cdot}$

Nitric oxide emitted to the troposphere from natural and anthropogenic sources follows a series of chemical reactions inter-converting NO, NO_2 and O_3 [Atkinson, 1995]. Reaction of NO_2 with O_3 leads to the formation of the nitrate ($NO_3^{\cdot}$) radical:

$$NO_2 + O_3 \longrightarrow NO_3^{\cdot} + O_2$$

The nitrate radical has a lifetime of approximately 5 seconds due to photolysis (for an overhead sun), hence concentrations remain low during daytime and increase to measurable concentrations during night-time [Atkinson et al., 1992; Atkinson, 1995].

Atkinson (2000) reports that measurements collected over the last 15 years indicate a night-time [$NO_3^{\cdot}$] at ground level over continental areas ranging from $<5 \times 10^7$ molecules cm^{-3} to 1×10^{10} molecules cm^{-3}.

It is believed that benzene is virtually unreactive to $NO_3^{\cdot}$. Studies conducted by Hjorth and co-workers (1997) have shown that $NO_3^{\cdot}$ initiated transformation of toluene and other alkyl benzene's begins with hydrogen abstraction from the alkyl group. Hjorth proposes that the product radical rapidly reacts with molecular oxygen, which eventually leads to the progressive oxidation of the organic matter.

The nitrate radical is anticipated to demonstrate a seasonal significance in the fate of BTEX aromatics. It is expect that during winter months, when daily averaged $[NO_3^{\cdot}]$ is believed to be at a maximum (due to low solar irriadinace), that the nitrate radical is most significant [Atkinson, 1990]. Additionally, wintertime daily averaged $[^{\cdot}OH]$ are expected to be approximately three orders of magnitude lower than typical mean summer time concentration.

The wintertime significance of each removal mechanism is explored further in Chapter 5 and 7.

2.4 SUSPENDED PARTICULATE MATTER

2.4.1 Introduction

This section presents the current scientific understanding of the physical and chemical properties of urban carbonaceous aerosol. In order that the Reader is aware of other aerosol species and convention for notation of particle size fractions, an introduction to tropospheric aerosol is provided below.

2.4.2 Physical Characteristics of Tropospheric Aerosol

2.4.2.1 Size and Number Distribution

In terms of physical and chemical properties, tropospheric aerosol is a very diverse material, and only recently has much of the chemical, physical and morphological features of anthropogenic, natural and biogenic particulate matter come to light.

It is not surprising that suspended matter can be found in a very wide range of particle sizes in the troposphere, when one considers the number and diversity of their sources [discussed extensively by Mathias-Maser (1998) and the Quality of Urban Air Review Group (1996)].

Atmospheric aerosol demonstrates characteristic size distribution, generally occurring in three modes [Jaenicke, 1998]:

- *Nucleation mode (ultrafine particles)*: The finest tropospheric particles, which are formed from the condensation of a small number of non-volatile molecules. They may be formed in combustion processes such as motor engines, and from gas to particle conversion where the product/s have a low saturated vapour pressure. Typical particle sizes in this range are 1-10nm, and demonstrate very high number density in urban atmospheres (10^5 to 10^6 particles cm^{-3} is common) [Quality of Urban Air Review Group, 1996].

- *Accumulation Mode (fine particles)*: Further condensation and coagulation of particles in the nucleation mode lead to the formation of long-lived particles roughly in the range of 0.05 to 2μm. Accumulation mode particles constitute a significant fraction of the total aerosol mass in urban atmospheres. Also, it is believed that Carbonaceous Combustion Aerosol (CCA) emitted by diesel vehicles constitutes a major fraction of the accumulation mode mass within urban areas [Williams et al., 1989].
- *Coarse Particles*: The third mode in the size distribution profile constitutes particles of approximate 10-100μm in diameter. This size fraction results mainly from the reduction of massive material to fragments, formation of sea spray, and other sources of wind blown dust and biogenic particles. Although the particle number density is typically small, coarse particles constitute significant fraction of the total aerosol mass [Quality of Urban Air Review Group, 1996].

2.4.2.2 Aerodynamic Diameter

As the morphology of atmospheric aerosol is very diverse, it is convenient to use the term 'aerodynamic diameter' (d_a) of a particle rather than the true diameter. This is defined as the diameter that the particle would have if it were to be spherical in shape, to be of unit density (1g cm^{-3}) and to have the same sedimentation rate.

The 'equivalent' diameter (d_e) is the diameter of a sphere having the same volume as the irregular particle and is given by:

$$d_e = \left(\frac{6V}{\pi}\right)^{1/3}$$

where V is the volume of the particle.

An extensive study by Rogge et al. (1993) of fine particulate mass collected in West Los Angeles and Rubidoux (Riverside), southern California, demonstrates the compositional diversity of tropospheric aerosol. A summary of this work is presented diagrammatically below.

Figure 2.3 Mass Balance of the Chemical Composition of Annual Mean Fine Particle Concentrations for (a) West Los Angeles and (b) Rubidoux (Riverside) [from Rogge et al., 1993]

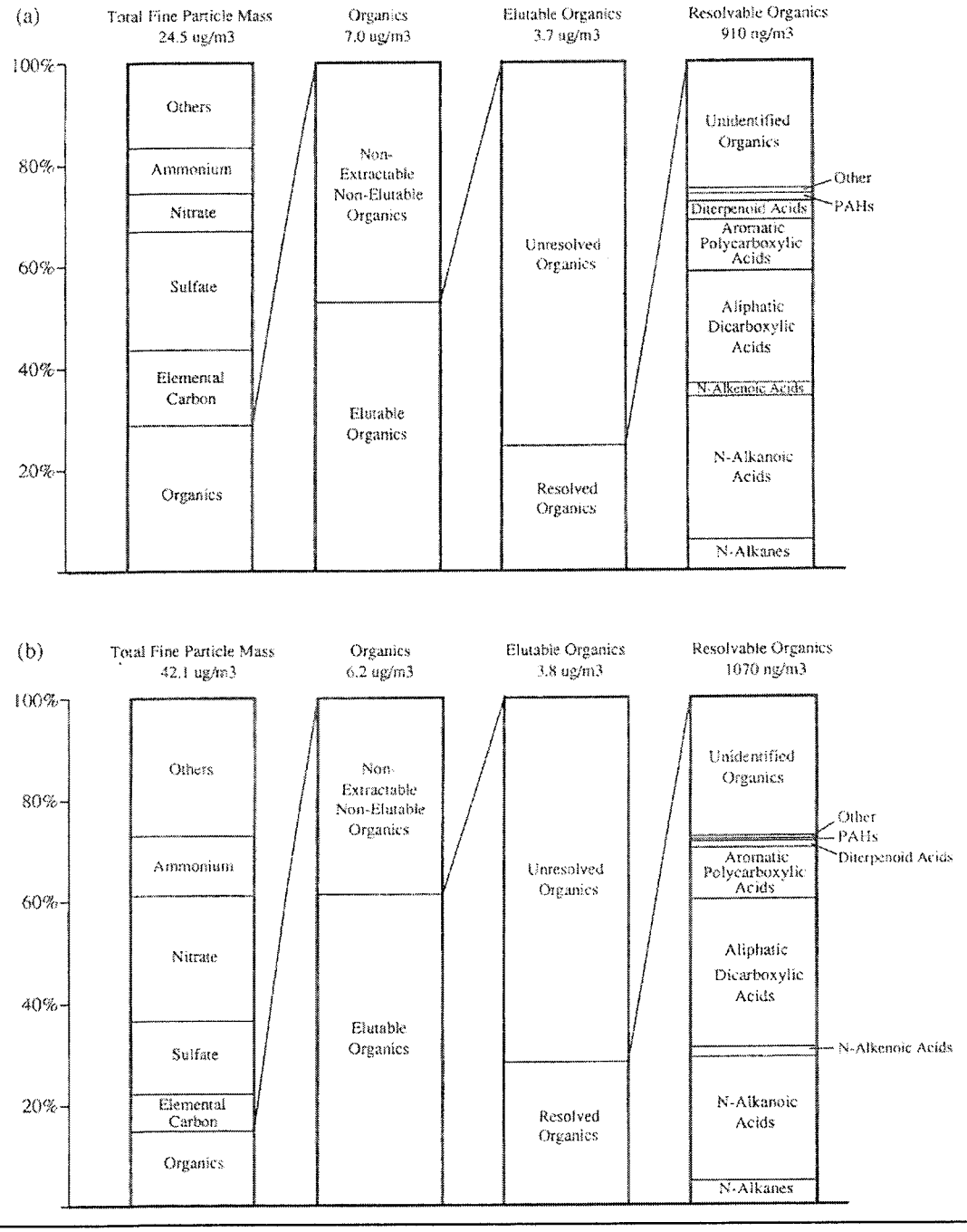


Figure 2.3 demonstrates the significant spatial variability of tropospheric aerosol composition, a feature noted by a number of authors [Quality of Urban Air Review Group, 1996; Penner and Novakov, 1996; Cachier, 1998]. Rogge's work also demonstrates that a significant fraction of tropospheric aerosol, particularly urban aerosol, is of a carbonaceous nature. Urban carbonaceous aerosol is discussed below.

2.4.3 Urban Carbonaceous Aerosol

2.4.3.1 Formation of Urban Carbonaceous Aerosol

Combustion of fossil fuels, such as diesel, results in the emission of reactive and unreactive gases, and aerosols [Goldberg, 1985]. Although combustion processes overwhelmingly account for carbonaceous aerosols in urban atmospheres, another recognised source is the oxidative conversion of organic gases (such as those emitted by living vegetation), which may be significant at certain localities [Rogge et al., 1993].

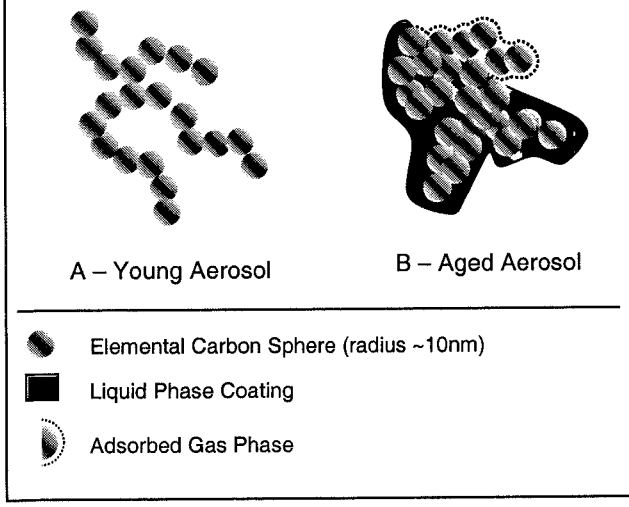
2.4.3.2 Composition of Diesel CCA

Several recent studies have identified two common features of diesel CCA:

- a 'core' component of Elemental Carbon (EC) associated with a polymerised and refractory involatile organic fraction known as Black Carbon (BC). Formation of the EC+BC core of combustion aerosol may be explained by the by polymerisation and dehydrogenation of the fuel under the oxidative action of the hydroxyl radical or any oxidant [Goldberg, 1985; Cachier, 1998]; and
- a coating of non-volatile and semi-volatile Organic Carbon (OC) fraction [Gundel et al., 1994] (discussed below).

Formation of CCA by diesel vehicles is believed to take place in three steps. Initially, only EC+BC particles are formed (later to become the 'core' component of diesel CCA), while VOCs and SVOCs associated with the fuel and engine oil are in the vapour phase. As the exhaust gas cools organic compounds condense or adsorb to the particle surface, and in addition, EC+BC particles coagulate [Bridleman et al., 1999]. The third step involves surface exchange of (predominately) organic gases during the lifetime of the particle. This latter process is a widely accepted phenomenon for a number of semi-volatile organic compounds (SVOC) [Williams et al., 1986; Williams et al., 1989; Eatough et al., 1995; Cachier, 1998]. After considerable exposure to the boundary layer, the particles are considered to be 'aged'. Figure 2.4 presents a postulated structure of both young and aged CCA from diesel vehicles [Adopted from Cachier, 1998].

Figure 2.4 Postulated Structure of Young and Aged CCA



2.4.3.3 OC Fraction of Carbonaceous Combustion Aerosol

Comprehensive characterisation of the OC fraction of traffic generated urban aerosol has been reported in only a handful of studies. This is perhaps because of the difficulties associated with the collection of a substantial, representative sample of

aged diesel aerosol, noted by a number of authors [Cronn et al., 1977; Appel et al., 1980; Grosjean, 1983; Rogge, 1993].

Earlier studies have shown several limitations:

- the majority of earlier work on diesel CCA has considered the range and composition of the OC fraction in terms of PAHs only [Williams, 1989; Quality of Urban Air Review Group, 1996];
- the occurrence and extent of an organic liquid phase associated with diesel CCA has not been explored to any great depth in earlier work;
- the process of absorption of organic gases to an organic liquid phase associated with CCA has received little recognition in earlier work – most studies describe the association of SVOCs with particulate matter by physical adsorption only; and
- where details are available, the methodological approach of many authors consists of extracting the organic carbon from collected aerosol samples using solvents such as acetone. Consequent GCMS analysis of the solvent extract would most probably have precluded BTEX and other volatile compounds from MS detection. This is due to the use of a 'solvent delay' in the MS detection programme, or because of the co-elution of such volatile analytes with the extracting solvent. In such cases, the presence of more volatile species within diesel CCA cannot be confirmed [Eatough et al., 1995; Kiss et al., 1997; Cachier, 1998; Novakov et al., 2000].

Eatough and co-workers (1995) showed that an average of 67% of carbonaceous aerosol from urban atmospheres consisted of extractable organic matter. Another study showed the extractable fraction of diesel aerosol to represent between 10-30% of the total carbon content [Clain, 1998]. In Clain's study, 3700 individual organic compounds were shown to be present upon a particular sample of diesel combustion aerosol, although only around 30% of this matter could be identified satisfactorily

[Cachier, 1998], the broad range of organic compounds agreeing with work by Rogge and co-workers (1993, see Figure 2.3).

Several studies, such as those conducted in Belgian cities in the late seventies, demonstrated that a wide range of aliphatic hydrocarbons, PAHs, oxygenates, aromatic acids, esters, and nitrogen containing aromatic compounds mainly comprise the OC fraction of urban aerosol [Cautreels, 1978; Cachier, 1998]. These findings have been corroborated by more recent studies, which have indicated that aliphatic hydrocarbons and aliphatic acids constitute the main components of the OC fraction of urban aerosol [Eatough, 1995].

2.4.3.4 Physical Features of Diesel CCA

CCA from vehicle exhausts tends to be bimodal, with particles of 7.5-50nm diameter (nucleation mode) consisting of either carbon spheres, or condensed liquid hydrocarbon droplets, and an accumulation mode of about 0.05-1μm diameter [Quality of Urban Air Review Group, 1996].

It is recognised that elemental carbon from vehicle combustion aerosol is fairly porous and has a high surface area to mass ratio. Studies have indicated mean surface areas to be of the order of $100m^2g^{-1}$ for gas fixation, and approximately half of this for liquid fixation [Schure et al., 1985], however these figures can only be taken as approximate due to the remarkable heterogeneity of combustion aerosol.

2.4.4 Sink Mechanisms of Tropospheric Aerosols

The smallest particles (of several nanometers) have the shortest lifetimes, lasting for several minutes before coagulating with other particles (i.e. being removed from this size range and not from the atmosphere). Accumulation mode particles have lifetimes of approximately 10 days in the lower atmosphere before being removed by wet deposition processes [Jaenicke, 1998]. In the absence of wet deposition

processes, particles in the accumulation mode could be airborne for up to 1000 days [Quality of Urban Air Review Group, 1996].

Coarser particles are removed rapidly by dry deposition, and demonstrate short lifetimes of about 10-20 hours. The rate of sedimentation is defined by Stokes Law, which relates the terminal settling velocity of a smooth, rigid sphere in a viscous fluid of known density and viscosity, to the diameter of the sphere when subjected to a known force field:

$$V = \frac{(2gr_e^2)(d_1 - d_2)}{9\mu}$$

Where: V = velocity of fall (cm sec^{-1});

g = acceleration of gravity (cm sec^{-2});

r_e = 'equivalent' radius of particle (cm), i.e. d_e*0.5;

d_1 = density of particle (g cm^{-3});

d_2 = density of medium (g cm^{-3}); and

μ = viscosity of medium (dyne sec cm^{-2}).

2.4.5 Sink Mechanism for Trace Atmospheric Species

It has been known for some time that SVOC's, such as PAHs, demonstrate a characteristic gas-particle distribution under various atmospheric environments [Jones et al., 1994; Lewis et al., 1994; Gundel et al., 1994; Yordanov, 1995]. However, the occurrence and significance of such distribution of relatively volatile species, such as the BTEX aromatics, is not well understood.

It has been acknowledged, however, in very recent research, that benzene and toluene have been detected within the OC of aged urban CCA and aerosol formed

from biomass burning [Cachier, 1998]. The extent and significance of gas / aerosol distribution of BTEX is explored in Chapter 6.

2.5 TRANSPORT AND DISPERSION OF BOUNDARY LAYER POLLUTANTS

2.5.1 Dispersion

The role of wind (i.e. the local pressure gradient), mechanical turbulence and thermal turbulence in the dispersion and dilution of primary pollutants has been reported earlier by Bunce (1998).

It is important to recognise that the processes of transport and dispersion of BTEX aromatics and particulate matter is essentially identical for each species.

Two separate measurements of wind direction and speed have been used in this research and it is important to acknowledge their difference:

- wind direction and speed of the local weather system (i.e. the prevailing pressure gradient); and
- wind direction and speed measured at the study site, which is representative of the micro-metrology associated with the study locality (which is heavily influenced by surface topography).

2.5.2 Diffusion

Diffusion is the net transport of a molecule in a gas (or liquid) and is a result of intermolecular collisions rather than turbulence or bulk transport. It is defined as:

$$D_{BA} = \frac{F_B}{\alpha X_B}$$

Where: D_{BA}= diffusion coefficient of compound B in medium A (in this study, air, $cm^2 s^{-1}$)

F_B= net molal flux of B across a hypothetical plane (mol $cm^{-2} s^{-1}$)

αX_B= concentration gradient of B at the hypothetical plane

(mol cm^{-2})

Although only playing a minor role in the migration and dispersion of pollutants in the boundary layer, the significance of diffusion is much greater in non-turbulent atmospheres, such as the isolated environment discussed in Chapter 7.

Due to the scarcity of experimental data, the Wilke and Lee (WL) model has been adopted for determination of diffusion coefficients of the BTEX aromatics in air [Wilke and Lee, 1955]. The WL model is reported to be useable for a wide range of compounds. According to Jarvis and Lugg (1968), the absolute average error for about 150 compounds tested was 4.3%, and aromatics had an average error of less than 8%.

Table 2.8 present modelled values of D_{BA} for the BTEX aromatics in air. The numerical approach of this model has been prepared upon a spread sheet, and is included upon the data disc provided with this Thesis (located inside of the back cover).

Table 2.8 Modelled Diffusions Coefficients of BTEX Aromatics in Air

$D_{BA}^{T(K)}$	Benzene	Toluene	Ethylbenzene	p-Xylene	m-Xylene	o-Xylene
D_{BA}^{273} ($cm^2s^{-1} \times 10^2$)	8.43	7.48	6.77	6.76	6.76	6.74
D_{BA}^{283} ($cm^2s^{-1} \times 10^2$)	8.90	7.89	7.14	7.14	7.13	7.11
D_{BA}^{293} ($cm^2s^{-1} \times 10^2$)	9.37	8.31	7.53	7.52	7.52	7.50
D_{BA}^{298} ($cm^2s^{-1} \times 10^2$)	9.61	8.53	7.72	7.71	7.71	7.69

All values derived using the Wilke and Lee Model (1955)

Modelled data indicates that there is very little difference between D_{BA} values of ethylbenzene and isomers of xylene. Benzene, however, has a notably higher D_{BA} value than the other BTEX aromatics.

2.6 RESEARCH AIMS

This chapter has demonstrated that the BTEX aromatics comprise a fairly unique and interesting group of tropospheric pollutants:

- there are no significant biogenic sources of BTEX aromatics [Field et al., 1992];
- in UK urban areas, BTEX aromatics predominately originate from road traffic emissions, the greatest fraction of this from petrol fueled vehicles [National Atmospheric Emissions Inventory, 1997];
- the *relative* long term average concentrations of each BTEX aromatic have been shown to remain approximately constant within traffic polluted atmospheres [Wathne, 1983];
- the chemical and physical behaviour of individual BTEX aromatics in the boundary layer is relatively diverse; and
- it is believed that the BTEX aromatics have only one significant sink mechanism, reaction with the hydroxyl radical [Atkinson, 2000].

Although strong experimental evidence exists to support the last point, other sink mechanisms have been identified and discussed within this chapter (summarised below in Table 2.9). It is clear from available literature that the effectiveness of any sink mechanism depends very much upon boundary layer physics, chemistry and meteorology, and therefore particular boundary layer environments may exist where sink mechanisms (other than BTEX transformation by ·OH radical) may become important.

Table 2.9	Description of other BTEX Sink Mechanisms	
Processes	**Description**	**Influencing factors**
Dry Deposition	As noted in Section 2.4, monoaromatic hydrocarbons have been detected within with the organic fraction of carbonaceous aerosol. As a sink mechanism, the surface exchange of BTEX aromatics upon carbonaceous particulate matter maybe important in particular environments.	Anticipated to be more significant in cold environments with high number density of carbonaceous aerosol (with significant liquid OC fraction)
Reaction with $NO_3^{\cdot}$	Although rates of reaction of BTEX aromatics with $NO_3^{\cdot}$ are slow, night-time concentrations of NO_3 have been shown to range over three orders of magnitude. Expected to be most significant in wintertime	Most significant in latitude's / seasons with weak solar flux.
Precipitation Scavenging	Expected to be a minor sink for gas phase BTEX, but significant for particles. If BTEX aromatics are appreciably distributed to particle bound organic phases, this deposition route may be important for BTEX aromatics	Anticipated to be most significant in cold environments with frequent precipitation

The aim of the research is to explore the significance of sink mechanisms of BTEX aromatics, other than their transformation by reaction with hydroxyl radical. These aims will be achieved through deconvolution of temporal trends within quasi-continuous measurements of BTEX aromatics within urban, suburban and isolated boundary layer environments. It is also the aim of this research to explore the role of CCA in the removal of BTEX from the boundary layer.

2.7 RESEARCH OBJECTIVES

The objectives are:

- to establish the ratio and ranked order of BTEX aromatics at kerbside and urban background locations, and to explore the consistency of these ratio's with time and proximity to road traffic;
- derive a surrogate measure of the photochemical potential of a traffic polluted atmosphere, using concentrations of inorganic gases;
- to utilise quasi-continuous measurements of BTEX aromatics at two different boundary layer environments. Data yielded from individual studies will be

subjected to statistical treatment to assist in the deconvolution of diurnally seasonal trends;

- to investigate aged CCA samples, to identify volatile components within an extractable organic fraction.
- to utilise quasi-continuous measurements of BTEX aromatics within isolated boundary layer environments, to investigate differential changes in BTEX aromatic concentrations in the absence of sunlight, precipitation, and significant mixing with the free boundary layer.

3 METHODOLOGY

The following chapter presents a critique of the analytical techniques applied in this investigation, principally Thermal Desorption – Gas Chromatography – Flame Ionisation Detector (TD-GC-FID) and Tapered Element Oscillating Microbalance (TEOM). Techniques applied by third parties for the collection of other data (such as inorganic gases, meteorology etc.) are discussed in Appendix 2.

Experimental and instrumental details regarding the characterisation of CCA are presented within Chapter 6.

3.1 SAMPLING AND ANALYSIS OF BTEX AROMATICS IN AMBIENT AIR

The analytical technique applied in this research permitted the cyclic, automated analysis of VOCs in ambient air. The system was optimised for the analysis of BTEX aromatics to achieve a temporal resolution of 48 measurements per day. The theory and general features of gas chromatography and flame ionisation detection have been discussed comprehensively elsewhere [Nikelly, 1986; Fowlis, 1995; Kitson et al., 1996].

3.1.1 Thermal Desorption Gas Chromatography Flame Ionisation Detector (TD-GC-FID)

The Chrompack CP70001 TD-GC-FID configuration and sampling sequence is summarised diagrammatically in Figures 3.1 and 3.2, and is described in further detail below.

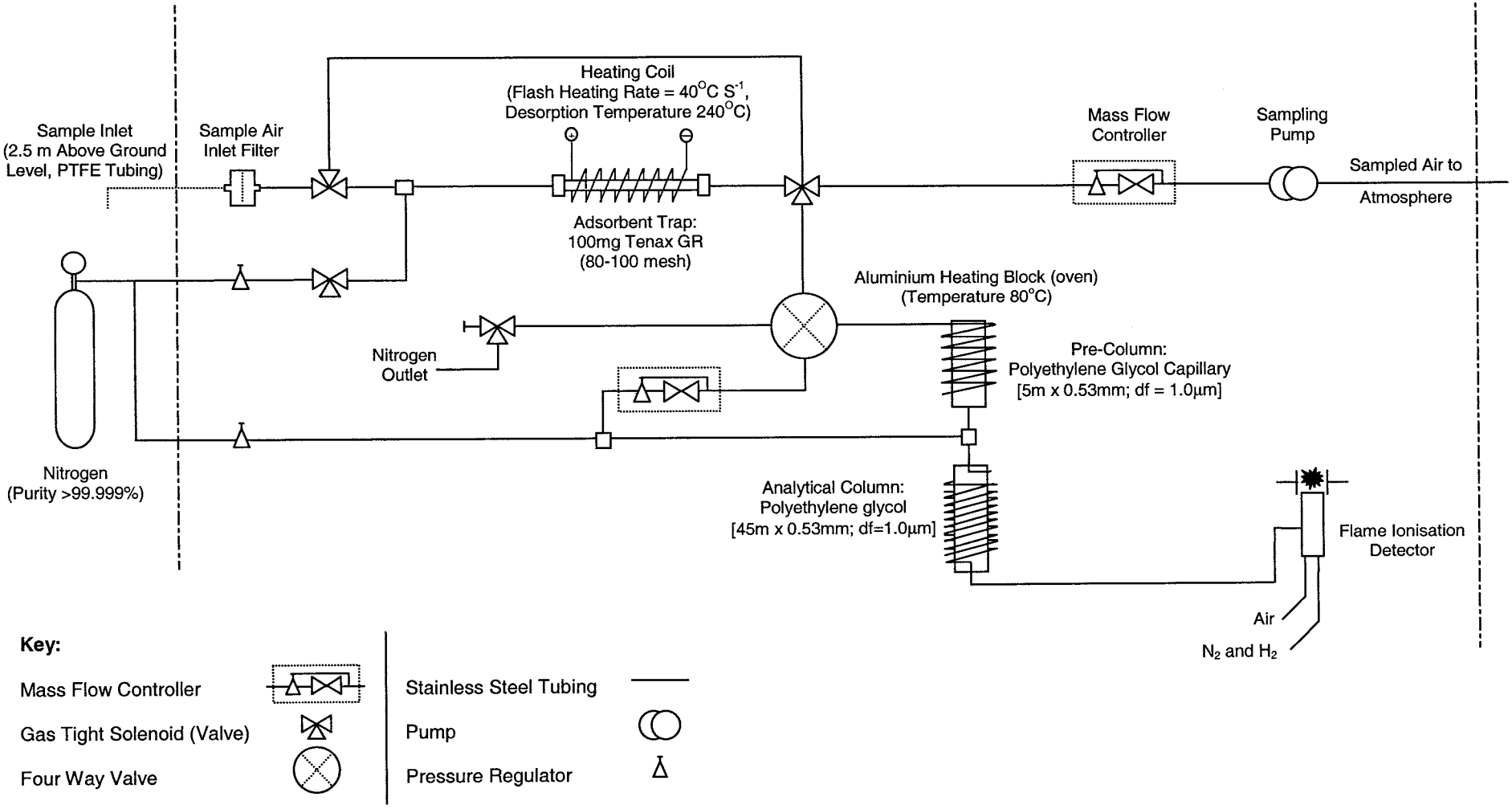
The sampling stage of the cyclic system involved passing 300ml of the sample atmosphere over a thermostatically controlled adsorbent bed of 100mg Tenax GR (a composite material of 70% poly-2,6-diphenylene oxide and 30% graphite; 80-100

mesh), at 40°C. The maximum sampling time used was 20 minutes for each measurement (required to achieve a temporal resolution of 48 measurements day^{-1}).

Sample and calibrant gas flow rates were regulated by means of a mass flow controller. Following completion of the sampling cycle, the adsorbent trap was then flushed with nitrogen, and rapidly heated (ca. 40°C s^{-1}) to 240°C, which achieved rapid or 'flash' desorption of adsorbed VOCs. Desorbed analytes were then transferred under a flow of carrier gas (cylinder nitrogen gas, purity >99.999%) to a capillary pre-column (polyethylene glycol capillary, 5m x 0.53mm; df = 1.0μm). The pre-column was back-flushed with carrier gas to remove undesired VOCs, before analytes were transferred to an analytical column (polyethylene glycol, 45m x 0.53mm; df=1.0μm). Separation was achieved isothermally (oven temperature 80°C).

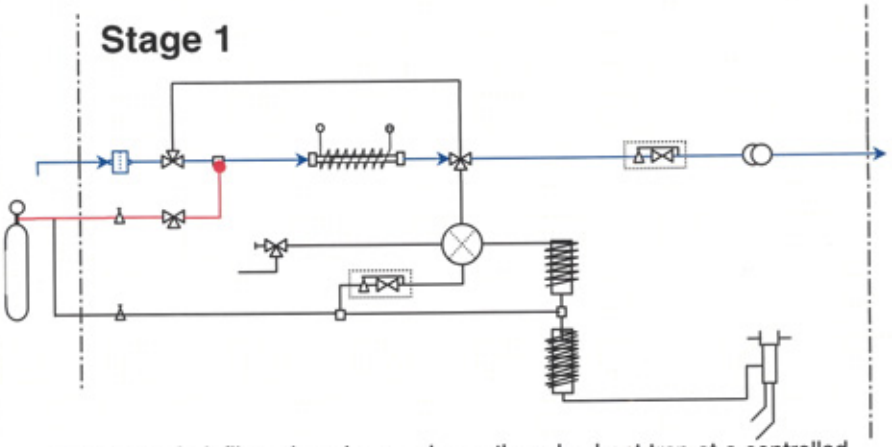
Detection of separated analytes was achieved by H_2 and air flame ionisation detector with N_2 makeup gas (H_2 and air generated by Peak Scientific hydrogen and clean air generators; purity >99.999%, N_2 purity >99.999%). Signals from the FID were integrated using Chrompack PCI software.

Figure 3.1 Configuration of the Cycle TD-GC-FID System

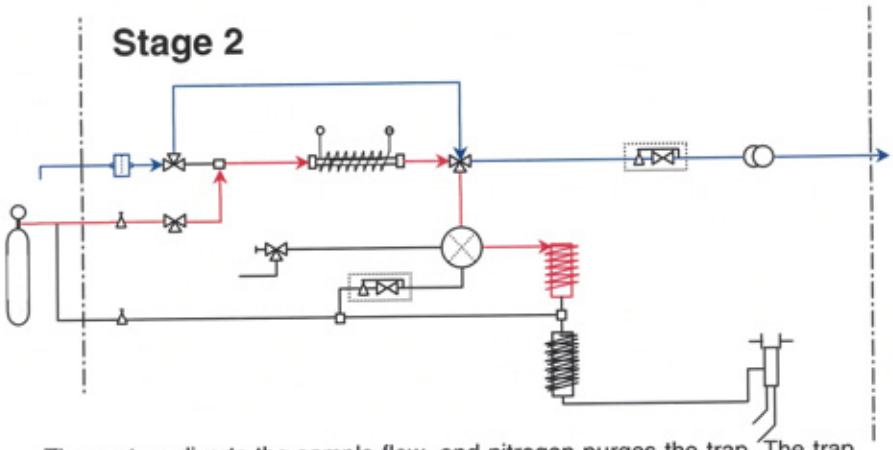


Adapted from Chrompack, 1993

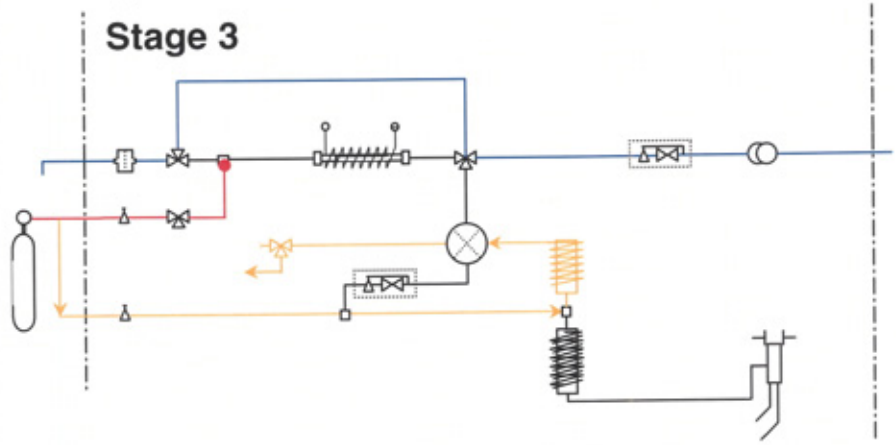
Figure 3.2 Operational Scheme of the Automated TD-GC-FID for Measurement of VOCs in Urban Air



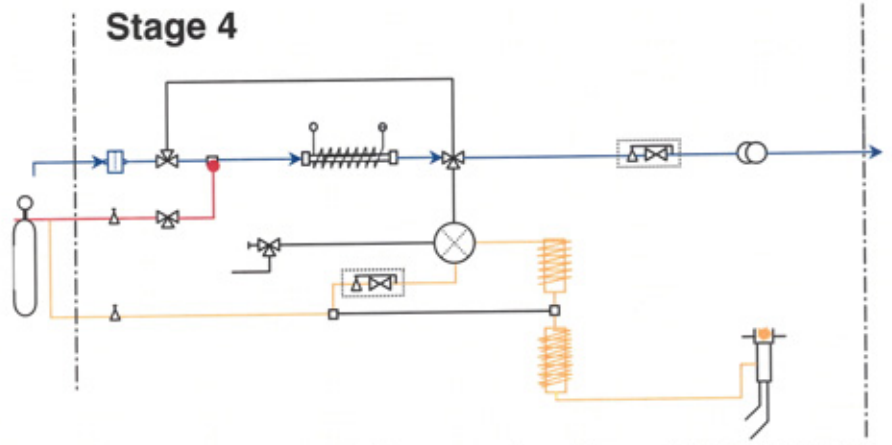
Air is sampled, filtered, and passed over the adsorbent trap at a controlled flow rate. Sampling time typically 15 minutes (normal sample volume of 300ml).



The system diverts the sample flow, and nitrogen purges the trap. The trap is heated rapidly and a flow of nitrogen transports desorbed analytes to a pre-column.



A counter flow of nitrogen is then applied to the pre-column, which back-flushes and removes higher boiling point compounds from the analyte matrix. The adsorbent trap cools.



The nitrogen carrier gas flow is then reversed, and the analytes are flushed to an analytical column where sample components are separated, and then passed to an FID for detection. Sampling resumes whilst separation and detection of the first sample continues.

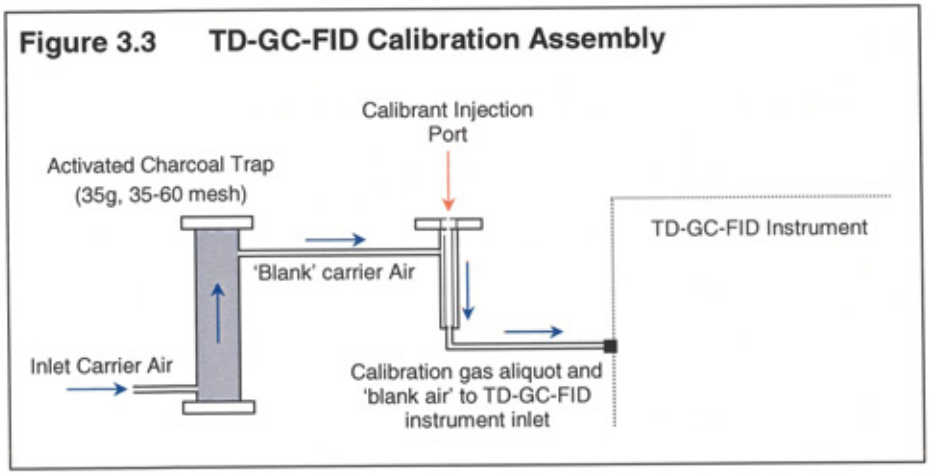
Adapted from Chrompack, 1993

3.1.1.1 Calibration

The system was calibrated by means of dilutions of commercial calibrant gases (Scott, National Physical Laboratory), which were prepared in Tedlar bags, by delivering aliquots of calibrant gas (by gas tight syringe) into known volumes of cylinder nitrogen (purity >99.999%) at 1 atmosphere and room temperature.

Aliquots of diluted calibrant gas were delivered to the adsorbent trap of the TD-GC-FID at a flow rate, temperature and sampling duration comparable to that used for ambient air samples. The delivery of aliquots of calibrant gases was achieved by gas tight syringe, to a modified sample inlet, which comprised an injection port and carbon trap, the arrangement of which is presented in Figure 3.3 below.

Figure 3.3 TD-GC-FID Calibration Assembly



3.1.1.2 Analytical Performance

Statistical analysis of the response to a fixed aliquot of calibrant gas is presented in Table 3.1. The concentration of BTEX aromatics within the calibrant gas had been determined to an accuracy of 2% by the supplier, and total measurement error associated with the determination of each analyte is presented below.

Table 3.1 Analytical Performance of TD-GC-FID

Parameter	B	Tol	EB	PX	MX	OX	ΣPMX
Retention Time(t_R, min)	5.2	6.4	8.4	8.8	9.0	10.4	8.8
Measured Concentration of Test Standard (ppb)	2.0	1.9	1.9	1.9	1.9	1.9	3.8
95% Confidence Interval (n=12, %)	1.7	1.3	1.9	9.8	18.9	2.1	3.9
Linearity of Response (r^2) [1]	0.997	0.998	0.997	0.971	0.934	0.998	0.997
Limit of Detection in 300ml sample (ppb) [2]	0.08	0.11	0.11	0.32	0.18	0.15	0.11
Accuracy of commercial calibrant gas (%)	±2.0	±2.0	±2.0	±2.0	±2.0	±2.0	±2.0
Total measurement accuracy (%)[3]	±5.0	±5.0	±5.0	±5.0	±5.0	±5.0	±5.0

ΣPMX = Sum of the concentrations of Para and Metaxylene

[1] Linearity of response to 0.1, 0.3, 1.0, 2.0, 3.4, 7.0 and 18ppb, 300ml sample. For each calibrant n=3, values are the square of the correlation coefficient (r);

[2] Limit of detection = $y_{BLANK} + 3\sigma_{BLANK}$; where y_{BLANK} = y axis intercept (a) of regression line, $\sigma_{BLANK} = \sigma_y/x$;

[3] Calculated using a linear combination of the accuracies of: the calibrant gas concentration, syringe, and stroke meter for standard dilution preparation (latter value estimated).

Para and metaxylene were found to co-elute, which resulted in considerable uncertainty in the integration of corresponding peak areas of either analytes. The summation of the peak areas of para and metaxylene was found to considerably improve the precision (by an average of 10%). Example chromatographs of calibrant and an atmospheric sample are presented below in Figures 3.4 and 3.5.

Figure 3.4 Chromatograph of 2ppb BTEX Standard (300ml Aliquot)

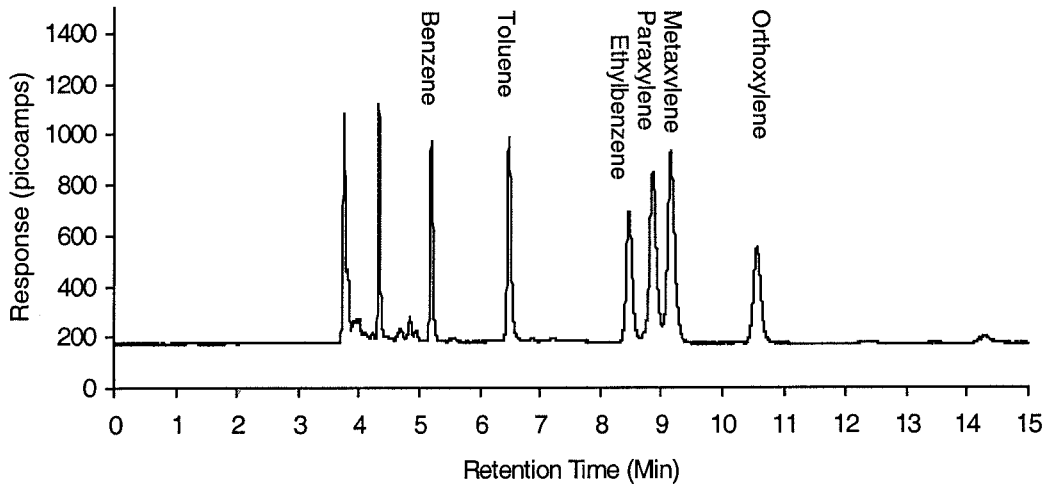
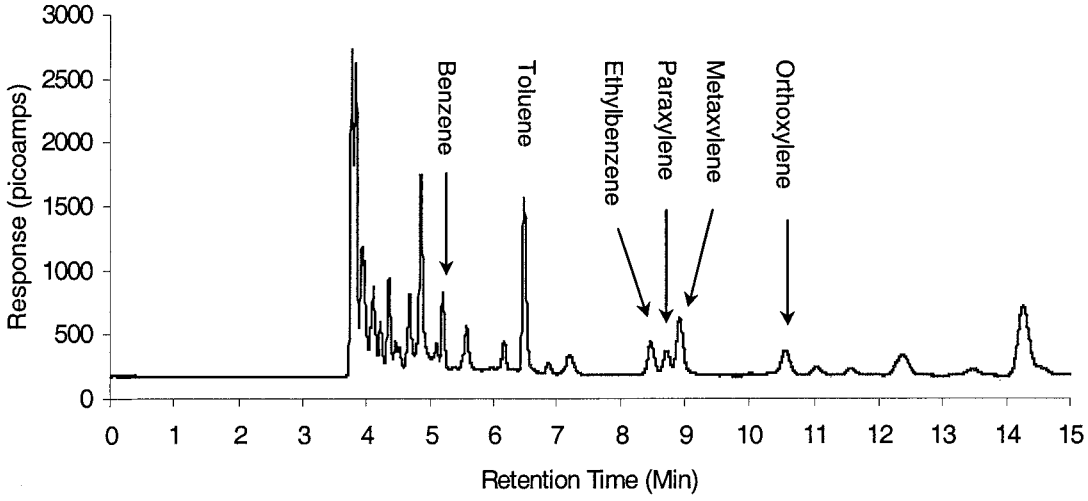


Figure 3.5 Chromatograph of 300ml Urban Air (Newcastle City Centre, 12.30pm, 9th November 1997)



3.2 SAMPLING AND ANALYSIS OF PARTICULATE MATTER

3.2.1 Introduction

The Rupprecht and Patashnick Tapered Element Oscillating Microbalance (TEOM) system is an ambient aerosol mass measurement system capable of real time measurement of the mass uptake upon a collection filter. The system comprises two components:

- a sampling device, which is responsible for size discrimination of ambient aerosol; and
- a microbalance (and associated control unit), which collects and records ambient aerosol mass with high temporal resolution.

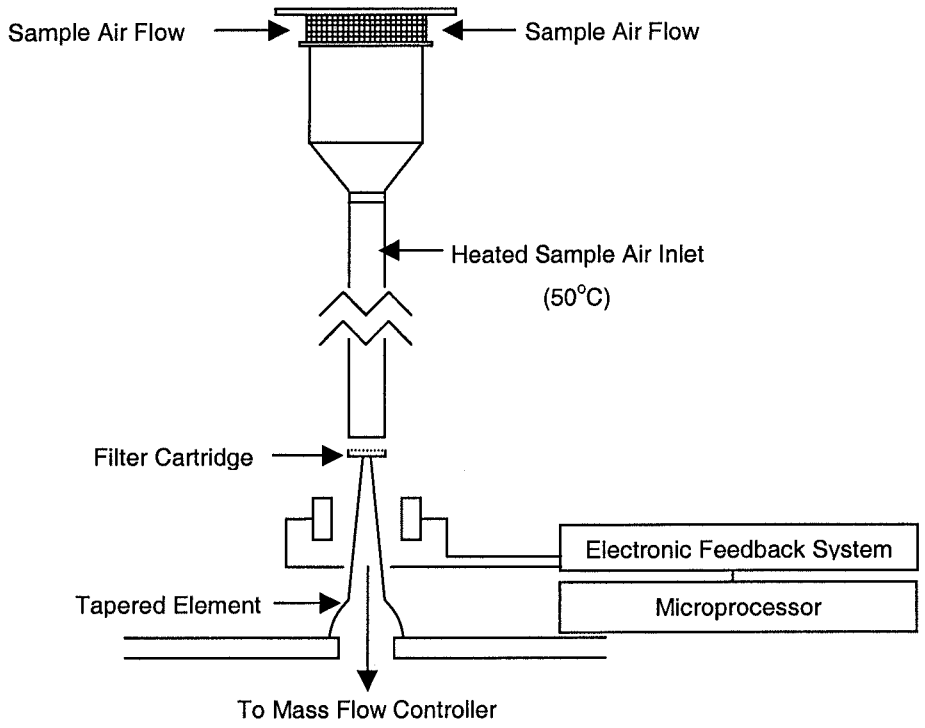
3.2.2 Principle of Operation

The theory of the TEOM's operation has been fully described previously [Shore and Cuthbertson, 1986], however a brief description is presented below.

The frequency of mechanical oscillation of an element such as a glass tube is directly proportional to the mass of the tube. Any consequent change of the tube mass is reflected in a change in its oscillating frequency [Patashnick and Rupprecht, 1991].

This principle is applied by the TEOM technique, where a filter rests upon the free end of a tapered glass element (see Figure 3.6).

Figure 3.6 Schematic Diagram of Rupprecht and Patashnick TEOM



As particulate mass collects upon the filter, the frequency of the tapered element changes proportionally. This change in frequency can then be translated to mass. This feature was described mathematically by Patashnick and Rupprecht (1991) through basic equations relating the frequency of oscillation (f), restoring force constant (k_r) and mass (m):

$$\omega = 2\pi f = (k_r/m)^{0.5}$$

or $$f^2 = K_o/m$$

Where:

ω = angular frequency of the motion;

m is defined as the total filter mass (m_F), the mass of the tapered element (m_0), and the particle loading (δm); and

$K_o = k_r / 4\pi^2$

The relationship between frequency and mass uptake has been shown to be a non-linear expression, however, this is not problematic as control software can manage such computation easily [Patashnick and Rupprecht, 1991]. The system is microprocessor controlled, and an electronic feedback system records the frequency of oscillation of the tapered element.

The TEOM inlet comprises an omnidirectional rain-protected entry followed by a size selective stage to discriminate between particulate matter with an aerodynamic diameter of 10μm (PM_{10}) and larger particles. Table 3.2 presents the sampling efficiency of the PM_{10} inlet for a range of aerodynamic diameters.

Table 3.2 Sampling Efficiency of the PM_{10} Sampling Inlet

Particle Aerodynamic Diameter (μm)	Overall Sampling Efficiency (%)
50.0	5
10.5	30
10.0	50
5.0	90
1.0	97

Adapted from Quality of Urban Air Review Group (1998)

Based upon the TEOM inlet's sampling efficiency, and the lower cut off of the collection filter (see below), the TEOM measurements will represent a range of aerosol materials. However, it also demonstrates that the TEOM's sampling and collection efficiency for accumulation mode diesel aerosol is very high.

3.2.3 TEOM Operation and Calibration

The TEOM instrument had been operated throughout this study with a PM_{10} selective inlet, which required a constant inlet flow rate of 16.7 L min^{-1} to achieve the desired particle size discrimination (Table 3.2).

The sample air flow rate was 3.0 L min^{-1}. The inlet and sensing assembly was maintained at 50°C, which is designed to remove water associated with ambient aerosol.

Atmospheric aerosols were collected upon a Teflon bonded borosilicate microglass fibre filter (13mm diameter collection surface, 99.6% collection efficiency of 0.035μm aerosols at 10cm s^{-1} face velocity). Changes in filter and tapered element mass were recorded every 13 seconds from which 30-minute averages were calculated. All data was recorded by a Rupprecht and Patashnick Data Storage Module, which processed and recorded signals from the sensing assembly.

3.2.3.1 Calibration

Calibration was achieved by means of pre-weighed masses (δm_{cal}). These masses were placed upon the surface of the filter. K_o (as defined above) can be derived from the frequency of the tapered element oscillation prior to (f_1) and following (f_2) the addition of a standard mass to the oscillator:

$$f_1^2 = K_0/(m_F + m_o)$$

$$f_2^2 = K_0/(m_F + m_0 + \delta m_{cal})$$

From these two equations, K_0 for a particular device can be determined:

$$K_0 = \frac{\delta m_{cal}}{(1/f_2^2) - (1/f_1^2)}$$

The TEOM system applied in this research was calibrated throughout by ETi Limited, Imperial House, No. 3 Montpellier Parade, Cheltenham, Gloucester GL50 1UZ.

3.2.4 Analytical Performance

The manufacturer claims that the working range of the 1400a Series TEOM is 0.1-1500 $\mu g\ m^{-3}$.

The precision of the instrument is 5% (cumulative uncertainty from pump flow rates, and calibrant masses [ETi Limited, Personal communication, 1998, 2000]. The sensitivity is 1.5$\mu g\ m^{-3}$ for a working range of 1-50μgm^{-3}.

3.2.4.1 Applicability of the Technique for Measurement of CCA

Allen and Reiss (1997) have expressed concern about the potential loss of volatile material from aerosol collected upon the TEOM's filter, resulting from the normal inlet and sensing assembly temperature of 50°C [Allen et al., 1997; Whitby et al., 1986;].

Allen and Reiss (1997) proposed that loss of water (associated with hygroscopic aerosol), ammonium nitrate, and organic semi-volatile material from the TEOM filter may lead to systematic differences in mass measurements of aerosol to other techniques. They do, however recognise in their report that highly volatile material, when present in significant amounts, leads to unpredictable and highly variable results in other aerosol collection methods.

The loss of particle-associate water induced by the TEOM's heated inlet and filter is intentional, and is required to provide a reference state for particle measurement, avoiding the need for measurement and consideration of tropospheric humidity [Patashnick and Rupprecht Co., Inc, 2000, personal communication].

Their proposition that organic matter is lost at the TEOM filter at 50°C appears unlikely to be significant in UK urban atmospheres, as thermogravimetric analysis of

urban CCA presented in Chapter 6, demonstrates very little mass loss below 100°C, findings which have been corroborated by other studies [Cachier, 1998].

Allen and Reiss indicated that loss of ammonium nitrate, through a shift in equilibrium between nitric acid and ammonia, appears to occur at the TEOM sampling temperature of 50°C. Upon review of their experimental data, this statement appears to be reasonable. As this research aimed to explore carbonaceous aerosol from road traffic, this feature does not raise particular concern.

Smith and co-workers (1997) indicated a good agreement between TEOM measurements and those collected by a Cascade Impactor (Graseby-Anderson) and an Automatic Cartridge Collection Unit (ACCU). However a systematic difference between the TEOM and conventional filter collection techniques has been recognised in this study (the TEOM demonstrated an under-representation of collected aerosol mass). This difference is adjusted by the factoring of all internally calculated data by the following formula, which has been determined experimentally [Patashnick and Rupprecht, 1991]:

$$Y=3.0+1.03x$$

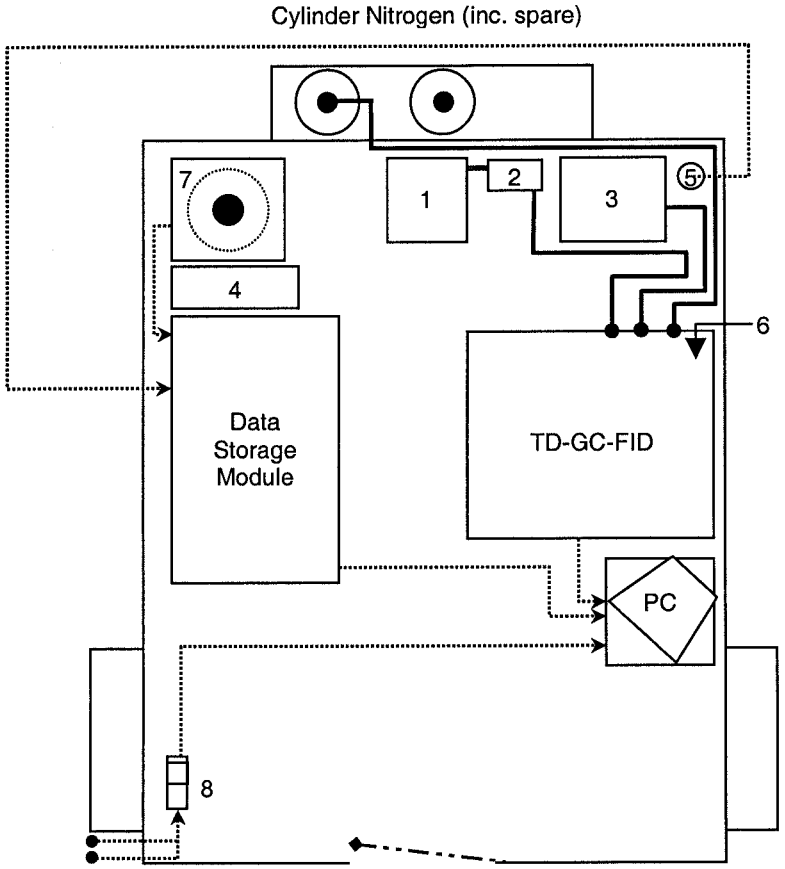
where x is of units μgm^{-3}

3.3 OTHER INFORMATION

3.3.1 Mobile Laboratory

The TEOM and TD-GC-FID were mounted within a Mobile Laboratory (ML), the layout of which is presented in Figure 3.7, with a number of images of the laboratory presented in Appendix 4 (Plates A4.1-A4.4).

Figure 3.7 Mobile Laboratory Scheme (Top View)



———	Steel gas line
·····→	Communication cable
1	Air compressor
2	Clean air generator (essentially a heated catalyst)
3	Hydrogen generator
4	TEOM pump and flow controller
5	Weather mast assembly, extendable to 10m above ground level, with mounted wind vane and anemometer
6	Sample Inlet for TD-GC-FID at 2.5m above ground level
7	TEOM sensor system. Sample inlet on top of laboratory roof at 3m above ground level (dotted outer circle)
8	Electronic thermometer and hygrometer (probe heights of 1m above ground level)

The ML provided a versatile means of monitoring within diverse localities, requiring only a source of power at each site to operate. The laboratory was deployed to sites of interest for periods of up to several months, depending upon the requirements of each investigation.

3.3.2 Analytical Data Disc

All analytical data from each of the investigations presented in the following chapters are included on a 3.5" data disc, located within the inside back cover of this document. The disc contains the following files in Excel format (Office 97):

SCC-studies.xls	Sunderland City Centre Studies (Chapter 4);
LT-studies.xls	Northumberland Street, Newcastle City Centre, and Church Street, Whitehaven Town Centre (Chapter 5); and
isol-env.xls	Bus Depot Study (Chapter 7).
WL Diffusion method	Wilke and Lee diffusion coefficient model

The first 'sheet' of each Excel file contains information about the relevant data set.

3.3.3 Third Party Measurements

A number of boundary layer measurements presented in later chapters were collected by third parties. Table 3.3 present's contributor information and measurement details.

Table 3.3 Third Party Measurements

Determinant	Provider	Address
Rainfall, humidity, boundary layer depth, wind speed, wind direction	The Met Office	Newcastle Weather Centre, 4th Floor, Portman House, Portland Road, Newcastle upon Tyne. NE2 1AQ.
Solar Flux	University of Northumbria	Northumberland Building, University of Northumbria, Newcastle upon Tyne. NE1 8ST
Schedule of bus movement	Northumbria Buses	Northumbria buses, 6 Portland Terrace Bus Depot, Newcastle upon Tyne. NE2 1QQ.
BTEX Concentration, Leeds and Middlesborough City Centres	Dept. of the Environment, Transport, and the Regions (DETR)	Eland House, Bressenden Place, London. SW1E 5DU.
Road Traffic Flow	Sunderland City Council	The business of the Environment Department, Sunderland City Council, Vurdon Road, Sunderland. SR2 7DN.
	Newcastle City Council	Division of Public Health and Environmental Protection, Newcastle City Council, Civic Centre, Newcastle upon Tyne. NE1 8PB.
	Copeland Borough Council	Main Office, Copeland Borough Council, Catherine Street, Whitehaven, Cumbria. CA28 7NY.
	Tyne and Wear Passenger Transport Authority	Tyne and Wear Passenger Authority, Civic Centre, Newcastle upon Tyne. NE99 2BN.

Appendix 2 presents methodological details of third party measurements.

3.4 STATISTICAL METHODS

This section provides details of statistical tests adopted for the analysis of data collected during the research, and describes the process of transformation of BTEX measurement data sets for statistical analysis in later chapters.

3.4.1 Elementary Statistics

Arithmetic mean (average), standard deviation (σ), confidence intervals (CI), and least squares linear regression have been discussed in a number of introductory texts [Gardiner, 1997]. Other statistical tools are discussed below.

Correlation Coefficient (r)

Correlation is a measure of the relationship between two or more variables. Correlation coefficients can range from -1.00 to +1.00:

- the value of -1.00 represents a perfect negative correlation;
- a value of +1.00 represents a perfect positive correlation; and
- a value of 0.00 represents a lack of correlation.

The type of correlation coefficient applied in this research is Pearson r, also called linear or product-moment correlation (noted as correlation hereafter), and determines the extent to which values of the two variables are 'proportional' to each other, the linear relationship being calculated by least squares regression.

The correlation coefficient is defined as:

$$Cov(X,Y) = \frac{1}{n}\sum_{i=1}^{n}(x_i - \mu_x)(y_i - \mu_y)$$

Outliers

Outliers are atypical (by definition), infrequent observations. Unfortunately, there is no widely accepted method to remove outliers automatically, however it is deemed necessary to apply a quantitative (and consistent) means of excluding outliers. It is considered acceptable to consider any data outside of ±3 standard deviations of the mean as outliers, unless otherwise indicated.

3.4.2 Frequency Distribution

3.4.2.1 Introduction

The distribution of many test statistics is normal or follows some form that can be derived from the normal distribution. The exact shape of the normal distribution (the characteristic 'bell curve') is defined by a function, which has only two parameters: mean and standard deviation.

Many environmental distributions are not normal. However, if the sample size is suitably large, the shape of the sample distribution approaches the normal shape, even if the distribution of the variable in question is not normal [Gardiner, 1997]. This principle is called the central limit theorem. For these reasons, it is deemed acceptable to apply elementary parametric tests to large data sets (n>100) presented hereafter.

Testing for Normality – Shapiro-Wilks' W Test

The Shapiro - Wilks' W normality test is the preferred test of normality because of its good power properties as compared to a wide range of alternative tests [Shapiro et al., 1968]. Monte Carlo simulation studies have indicated that the Shapiro - Wilks test has good power properties for a wide range of alternative distributions, and is more applicable to data sets of n >50 and <2000, than the Kolmonov – Smirnov test.

The 'W' statistic is a measure of the straightness of the normal probability plot, and values range between 0-1. Small values indicate a departure from normality.

3.4.2.2 Characterising Nonparametric Distributions

There are two means of quantitatively describing the 'shape' of a sample data set: Skewness, and Kutosis, both of which are described below.

3.4.2.3 Skewness

Skewness characterises the degree of asymmetry of a distribution around its mean:

- positive skewness indicates a distribution with an asymmetric tail extending toward more positive values; and
- negative skewness indicates a distribution with an asymmetric tail extending toward more negative values

(relative to the standard normal distribution, for which the skewness is 0). Skewness is defined as:

$$\text{Skewness} = \frac{n}{(n-1)(n-2)} \sum \left(\frac{x_j - \bar{x}}{\sigma} \right)^3$$

Where:

x_i = is the score for the i^{th} valid case

σ (sigma) = estimated standard deviation for the respective variable (computed as the square root of the sums of squares divided by n-1)

3.4.2.4 Kurtosis

The kurtosis is a measure of how 'wide' or 'thin' ('broad' or 'peaked') the distribution is for the respective variable, relative to the standard normal distribution (for which the kurtosis is equal to 0). It is also sometimes referred to as the fourth moment of the distribution.

Kurtosis is defined as:

$$\text{Kurtosis} = \left[\frac{n(n+1)}{(n-1)(n-2)(n-3)}\sum\left(\frac{x_i-\bar{x}}{\sigma}\right)^4\right]-\left(\frac{3(n-1)^2}{n-2(n-3)}\right)$$

3.4.3 Time Series Analysis

A time series is a collection of observations made sequentially in time. Time series analysis, in its simplest terms, involves some form of filtering of random noise (error) to make temporal patterns more salient.

The absolute concentration of BTEX aromatics, and indeed all other traffic related primary pollutants, undergoes relatively large variation throughout a daily cycle, through changes in emission rates (i.e. traffic density), and dispersion processes. Isolation of other, more subtle temporal trends which may described the boundary layer behaviour of aromatic hydrocarbons requires that these major systematic variations are effectively ignored.

A means of eliminating large diurnal variation of BTEX concentration is to consider the time series of *ratios* of the concentrations of aromatic hydrocarbons, as their rates of dispersion are identical, and their rates of emission remain approximately proportionally constant in traffic polluted atmospheres. The latter point has been confirmed through monitoring at kerbside sites during this research (discussed in Chapter 4) and by Nelson and Quigley (1982).

However, even the use of ratio's does not offer complete confidence in trends noted on, say, a single day, due to the fairly large *random* variation in ratio values. Therefore consideration of the time series over the daily cycle has been given to *net* diurnal seasonality recorded over n days. The process by which data sets have been transformed to permit this is described below, as well as the notation adopted for description of transformed time series.

3.4.3.1 Data Transformation Methodology

It is essential at this stage to fully understand the process of transformation of BTEX (and other) measurements, which will appear in later chapters of this Thesis:

1. If data for a single determinant is unavailable (e.g. through non-integration of a peak), all data collected for that time period of that day is removed (a 'time period' is 1 of 48 thirty-minute averaged measurements of the daily cycle);
2. Ratios of the remaining measurements are calculated. Almost exclusively, benzene will be used as the 'reference' species from which concentration ratios with other BTEX aromatics will be calculated, because benzene demonstrates the longest boundary layer lifetime, and has the smallest range of tropospheric sources in the UK (see Table 2.1 and 2.5). Ratios may also be calculated between individual aromatic hydrocarbons and the sum of BTEX aromatics for each time period;

3. The total BTEX aromatic concentration for that time period, denoted Σ [BTEX], is also calculated;
4. Outliers are removed (following the criteria discussed previously);
5. Ratio's for part or all of a study are grouped into one of 48 'categories', for each half-hour period of each measurement day (therefore if you transform 5 days of measurements, at 48 measurements per day, a sorted data set will have 5 measurements at 2200hrs, five at 2230hrs etc.). Outliers are removed;
6. Ratios for each time period are averaged, their standard deviation calculated;
7. The averaged ratios are smoothed using a moving average as described below, with typical aggregates of 3-5 periods; and
8. Moving averages of ratio's are then presented graphically against time of day, and subject to visual interpretation and linear regression analysis.

3.4.3.2 Notation of Transformed Data Series

Many such transformed series of data will emerge in following chapters, and it is necessary to adopt systematic notation of ratio values so that clarity is afforded to the Reader throughout this document.

The arrangement of this notation can be understood by example: say 10 days of data has been subjected to the transformation process described above. If the benzene / toluene concentration ratio for 2200 hours from this transformed data set is referred to, it shall be noted as:

$$[B/Tol]_{(2200)}$$

Where B = Concentration of Benzene at time T

Tol = Concentration of toluene at time T

2200 = Time, T

If a *series of ratios* is presented for a number of time period's e.g. 2200, 2230, 2300, 0000, and 0030 hours, then the *series* is denoted:

$[B/Tol]_{(2200\text{-}0030)}$

If a series for the complete diurnal cycle is presented, it is denoted:

$[B/Tol]_{(TOTAL)}$

Notation for other aromatics shall be performed as follows:

[EB]	[ethylbenzene]
ΣPMX	Σ([paraxylene]+[metaxylene])
OX	[orthoxylene]
Σ[BTEX]	Sum of the concentrations of the BTEX aromatics.

3.4.3.3 Data Smoothing

Smoothing always involves some form of local averaging of data such that the nonsystematic components of individual observations cancel each other out. The most common technique, which has been applied in this research, is moving average smoothing which replaces each element of the series by either the simple or weighted average of P surrounding elements, where P is the width of the smoothing 'window' [Box & Jenkins, 1976; Velleman & Hoaglin, 1981]. In all cases, unless noted otherwise, simple averages are used.

3.5 INTRODUCTION TO THE SITES OF INVESTIGATION

A number of diverse measurement localities have been selected for this research. Although these sites are discussed in the following chapters, to aid the Reader, a brief introduction to each is provided below in Table 3.4.

Table 3.4 Introduction to the Study Sites

Site Name & Location	Site Type [1]	Features	Areas of Investigation
Fawcett and Holmeside Street, Sunderland City Centre, Tyne and Wear.	Kerbside / Urban Background	Two separate investigations prior to and following pedestrianisation of a major street. Involved additional spectroscopic measurements of a number of inorganic gases	• Consistency of relative concentrations of BTEX • Temporal trends and ranked order of individual BTEX aromatics • Temporal correlation of BTEX with other primary pollutants and ozone
Northumberland Street, Newcastle City Centre.	Roadside	A long term wintertime study of diurnal concentration profile of individual BTEX aromatics	• Temporal trends in relative concentration of individual BTEX • Relationship of such trends with atmospheric temperature, wind vector, [PM_{10}] and traffic composition • Effect of precipitation upon relative BTEX concentration
Church Street, Whitehaven Town Centre, Cumbria.	Suburban Roadside	A long term wintertime study of diurnal concentration profile of individual BTEX aromatics	• To explore the coherency of relationships identified in the data collected from Northumberland Street
Tyne Tunnel, North Shields, Tyne and Wear.	Road Tunnel (roofing spaces)	A separate study involving the sampling and characterisation of the composition of settled carbonaceous aerosol	• Collection of large sample masses of settled carbonaceous aerosol within a road tunnel • Speciation of the organic carbon fraction of sampled matter • Upon these findings, speculation of the potential for absorption of BTEX into the organic liquid phase associated with carbonaceous aerosol
Northumbria Bus Depot, Portland Terrace, Newcastle upon Tyne.	Isolated Environment / urban background	A medium term study of BTEX aromatic concentration within a bust depot, an environment effectively isolated from the free boundary layer for long periods of the daily cycle.	• To explore the chemical and physical behaviour of BTEX aromatics within an isolated boundary layer environment • Exploration of collected data for evidence of uptake of BTEX upon diesel aerosol

[1] Classifications of 'site type' is described in Appendix 5. It is recommended that the unfamiliar reader aquatint themselves with convention for notation of 'site type'.

4 SUNDERLAND CITY CENTRE STUDY

4.1 INTRODUCTION

This chapter presents and interprets the findings of a study conducted within the city centre of Sunderland, Tyne and Wear, during 1996-1997. This Sunderland City Centre (SCC) study involved the ground-based measurement of [BTEX] and [PM_{10}] at two sites, prior to, and following the implementation of a road traffic management scheme along a busy road within the city centre.

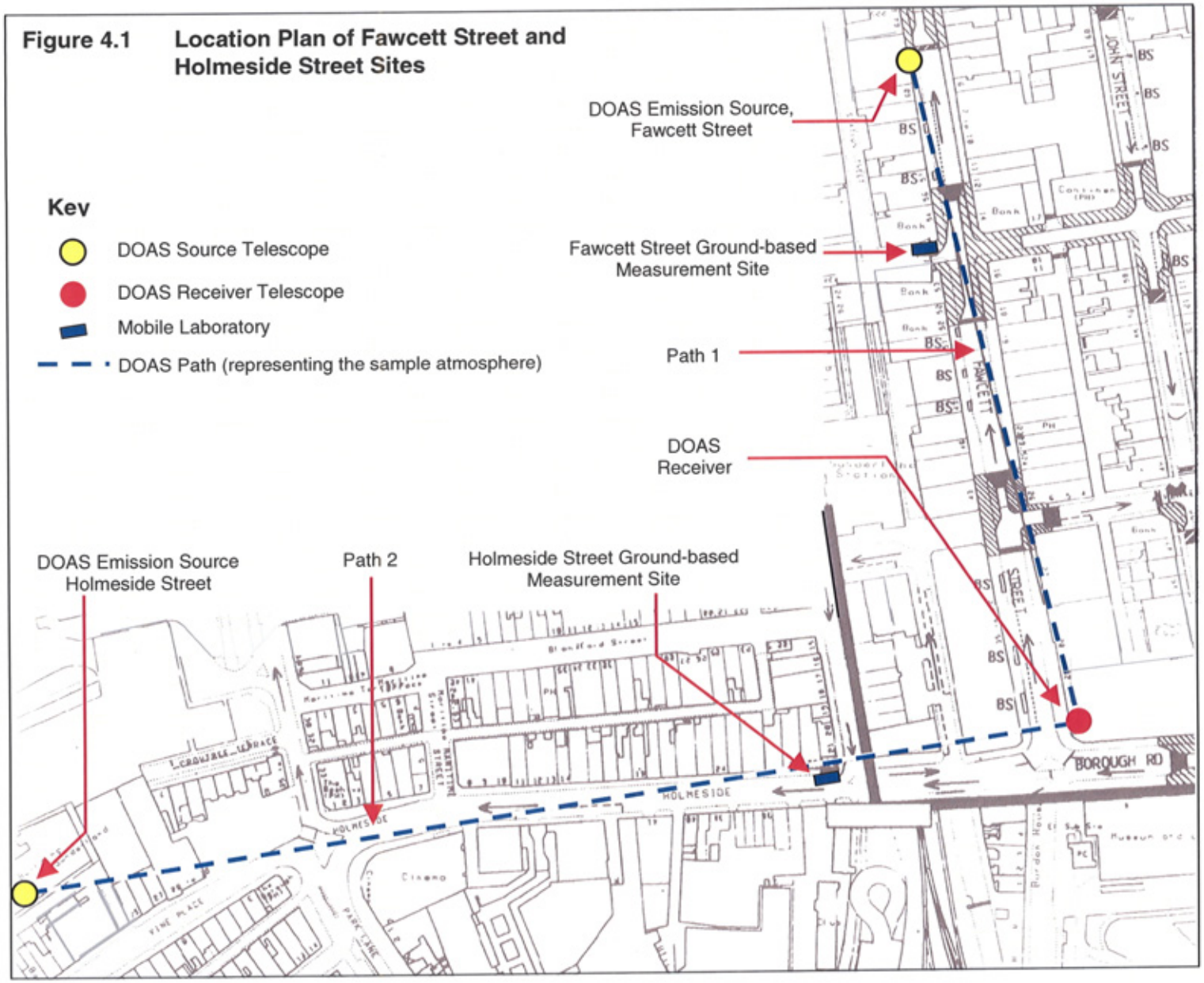
In addition to ground-based collection of data, near real-time spectroscopic measurements of the concentration of sulphur dioxide, nitrogen dioxide, and ozone were collected using two OPSIS / DOAS systems situated above each ground-based site at rooftop height.

4.2 DETAILS OF THE TRAFFIC MANAGEMENT SCHEME AND STUDY SITES

Sunderland is located on the north-east coast of England, and lies approximately 8 miles south east of Newcastle upon Tyne. At the time of this study, SCC received a high daily flow of road traffic, which represented the dominant source of BTEX aromatics within the city (emission of BTEX from nearby industrial sources was unlikely to have been significant within the city centre).

Between February 1996 and January 1997, a traffic management scheme was implemented at Fawcett Street. The scheme served to restrict the flow of road traffic along the street to commercial vehicles only (see Figure 4.1). Prior to the scheme, Fawcett Street experienced an average of 180 vehicles per hour, which was reduced to <50 vehicles per hour following the scheme. Nearby streets, such as Holmeside Street, were largely unchanged by the traffic management scheme (an estimated averaged traffic flow of 180 vehicles per hour at Holmeside Street).

Figure 4.1 **Location Plan of Fawcett Street and Holmeside Street Sites**



4.3 MEASUREMENT DETAILS

The study sites are described in detail below, however, a summary of data collection is provided in Table 4.1.

Table 4.1 Summary of Study Sites

Site Name	Locality Description [1]	Measurement Dates	n[BTEX / DOAS] / Cap (%)[2]	Other Measurements [3]
Ground Based Measurements				
Fawcett Street, Phase I	Urban kerbside	08-10.01.96	44 / 100	WS, WD, AT, PM_{10}, SF[4], RF[5], RTF[6]
Holmeside Street, Phase I	Urban kerbside	11-12.01.96	28 / 100	
Fawcett Street, Phase II	Urban, background	17-19.02.97	44 / 100	
Holmeside Street, Phase II	Urban kerbside	20-21.02.97	44 / 100	
Roof Top Measurements				
Fawcett Street, Phase I	Urban, 30m AGL	08-12.01.96	116 / 98	NO_2, SO_2, O_3
Holmeside Street, Phase I	Urban, 30m AGL	08-12.01.96	120 / 100	
Fawcett Street, Phase II	Urban, 30m AGL	17-21.02.97	118 / 99	
Holmeside Street, Phase II	Urban, 30m AGL	17-21.02.97	120 / 99	

[1] See Appendix 5 for locality class definitions, AGL = Above Ground Level

[2] Number of measurements of BTEX for ground-based sites, and DOAS measurements at rooftop sites / mean data capture. Data capture for individual BTEX is presented in Table 4.2

[3] WS =Wind Speed; WD =Wind Direction, AT = Air Temperature, SF = Solar Flux; RF = Rainfall; RTF =Road Traffic Flow

[4] SF measurements collected by The University of Northumbria, Newcastle upon Tyne

[5] RF measurements collected by The Met. Office, Newcastle upon Tyne

[6] RTF estimates provided by Sunderland City Council

4.3.1 Ground-Based Measurement of [BTEX] and [PM_{10}]

Two ground-based measurement sites were chosen for this study (indicated on Figure 4.1). The first site was located at Fawcett Street, the second at Holmeside Street. Measurements were collected at both sites at two stages: January 1996, prior to the implementation of the scheme ('Phase I'), and February 1997, following the

implementation of the scheme ('Phase II'). Holmeside Street was considered a kerbside site both before and after the traffic management scheme. Fawcett Street was considered a kerbside site before the implementation of the traffic management scheme (Phase I), however it was considered an urban background site in February 1997 (Phase II).

Measurement of [BTEX] and [PM_{10}] was achieved using TD-GC-FID and TEOM respectively (their operation was as described in Chapter 3). The ML was deployed and operated during daytime hours only (approximately 8am – 6pm), on midweek days. The ML was deployed to the same positions at both sites during both Phase I and II study periods.

4.3.2 Rooftop Measurements of [SO_2], [NO_2], and [O_3]

Concurrent measurements of [NO_2], [SO_2] and [O_3] were also collected at roof top level along Holmeside and Fawcett Street by Differential Optical Absorption Spectroscopy (DOAS). DOAS is a widely used technique for the unattended analysis of a number of tropospheric gases [Perner et al., 1979; Killinger and Mooradian, 1983]. The operation and calibration of the technique is discussed in Appendix 2.

4.3.2.1 Experimental

Rooftop measurements were achieved using an OPSIS AR 500 DOAS system. The system consisted of a light source (a 150 watt high pressure xenon lamp; beam divergence of 2 millirads), a receiving telescope (collection window diameter of 205mm, parabolic mirror focal length of 640mm), and a signal processing unit (spectrometer).

Although concern has been expressed earlier regarding the validity of DOAS measurements of aromatic hydrocarbons (Section 2.1), a number of studies have studies shown an excellent agreement between DOAS measurements of NO_2, SO_2 and O_3 with concurrently operated fixed point measurements by methods based upon

different physicochemical principles [Taubenberger, 1989; Conner and Stevens; 1991; Stevens et al.; 1993; Graber et al., 1994].

The Division of PHEP, Newcastle City Council, was responsible for the installation of the DOAS systems during this study. The DOAS paths were oriented as follows (Figure 4.1):

- Path 1 longitudinally intersected Fawcett Street, with a path length of 240 m, at 30m above ground level; and
- Path 2 longitudinally intersected Holmeside Street, with a path length of 320 m, at 30 meters about ground level.

Both DOAS systems operated continuously during between the study dates indicated in Table 4.1, reporting hourly average concentrations for each analyte.

4.4 RESULTS

4.4.1 Kerbside Measurements

4.4.1.1 Descriptive Statistics

A statistical summary of ground based measurements is presented in Table 4.2 below.

Table 4.2 Statistical Summary of Ground-Based Measurements

Parameter	B (ppb)	Tol (ppb)	EB (ppb)	ΣPMX (ppb)	OX (ppb)	PM_{10} (μgm^{-3})
Fawcett Street, Phase I Study						
No. Results (n) / Cap (%)[1]	44/100	44/100	44/100	44/100	44/100	42/100
Mean	4.5	10.6	2.9	6.9	3.2	43.8
Mean Proportion[2] (%)	15.9	37.7	10.5	24.5	11.3	
Maximum	7.9	19.2	5.0	10.8	5.8	151.0
Fawcett Street, Phase II Study						
No. Results (n) / Cap (%)[1]	44/100	44/100	44/100	34/77	27/61	44/100
Mean	1.5	2.2	1.2	0.3	0.3	15.7
Mean Proportion[2] (%)	26.5	40.1	22.2	6.1	5.1	
Maximum	4.5	4.4	1.7	1.2	2.2	29.5
Holmeside Street, Phase I Study						
No. Results (n) / Cap (%)[1]	29/100	29/100	29/100	29/100	29/100	29/100
Mean	2.2	5.3	1.5	3.2	1.5	34.4
Mean Proportion[2] (%)	16.1	38.5	11.1	23.2	11.1	
Maximum	3.1	8.7	5.4	6.4	3.2	59.5
Holmeside Street, Phase II Study						
No. Results (n) / Cap (%)[1]	29/100	29/100	29/100	29/100	29/100	29/100
Mean	2.2	5.6	1.6	2.5	1.2	23.4
Mean Proportion[2] (%)	12.5	35.3	16.0	24.3	11.9	
Maximum	3.7	7.3	2.5	3.2	1.6	39.5

[1] Number of measurements above limit of detection / % data capture

[2] Mean proportion, or $\alpha[BTEX] = \left(\frac{\bar{x}[BTEX]}{\bar{x}\Sigma[BTEX]}\right) x100$

The ranked order of net mean [BTEX] values in Table 4.2 demonstrates reasonable consistency amongst those sites defined as kerbside: (highest mean concentration

first) toluene > Σpara+metaxylene > benzene > orthoxylene ≈ ethylbenzene. This distribution agrees with the ranked order of mean [BTEX] reported for petrol vehicle emissions in the UK (see Table 2.1).

Chart 4.1 presents the daytime concentration profiles of [BTEX] during the Phase I study. Chart 4.2 presents daytime Σ[BTEX] and PM_{10} measurements for Phase I data.

Chart 4.1 Daytime Concentration Profile of BTEX, Phase I

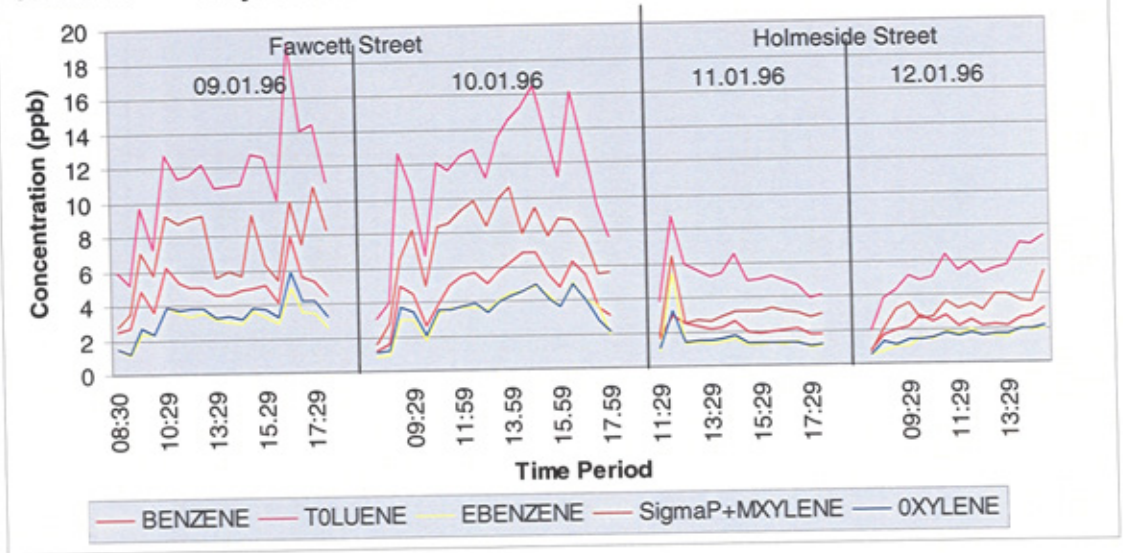
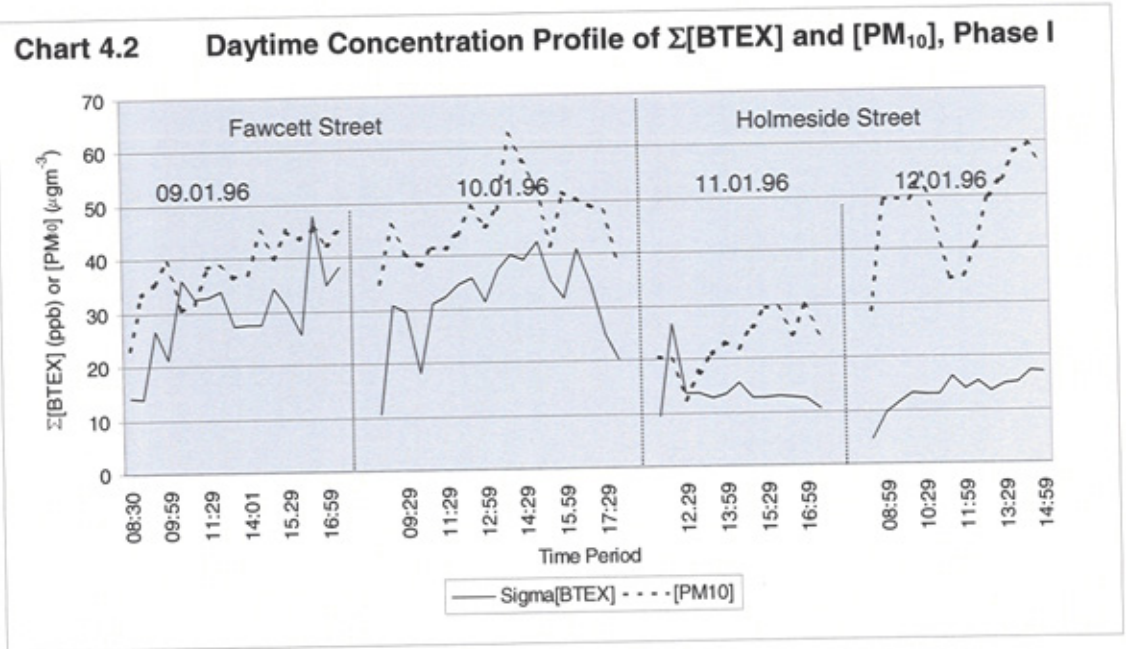


Chart 4.2 Daytime Concentration Profile of Σ[BTEX] and [PM_{10}], Phase I



The charts indicate a strong, positive intercorrelation between individual aromatics, suggesting a common source dependence for each species.

4.4.1.2 Ratios of [BTEX] and [PM_{10}]

Ratios of the mean concentration of individual aromatics and PM_{10} at each site are presented in Table 4.3.

Table 4.3 Mean [BTEX] and [PM_{10}] Ratios

Fawcett Street

	Phase I						Phase II						
Phase I	B	Tol	EB	ΣPMX	OX	PM_{10}	Phase II	B	Tol	EB	ΣPMX	OX	PM_{10}
B		0.4	1.5	0.6	1.4	0.1	B		0.7	1.2	4.5	5.2	0.1
Tol	2.4		3.6	1.5	3.3	0.2	Tol	1.5		1.8	6.8	7.8	0.1
EB	0.7	0.3		0.4	0.9	0.1	EB	0.8	0.6		3.8	4.3	0.1
ΣPMX	1.5	0.6	2.3		2.2	0.2	ΣPMX	0.2	0.1	0.3		1.1	<0.1
OX	0.7	0.3	1.1	0.5		0.2	OX	0.2	0.1	0.2	0.9		<0.1
PM_{10}	9.8	4.1	14.9	6.4	13.8		PM_{10}	10.6	7.0	12.7	47.6	54.7	

Holmeside Street

	Phase I						Phase II						
Phase I	B	Tol	EB	ΣPMx	OX	PM_{10}	Phase II	B	Tol	EB	ΣPMx	OX	PM_{10}
B		0.4	1.5	0.7	1.4	0.1	B		0.4	0.8	0.5	1.1	0.1
Tol	2.4		3.5	1.7	3.5	0.2	Tol	2.8		2.2	1.5	3.0	0.2
EB	0.7	0.3		0.5	1.0	<0.1	EB	1.3	0.5		0.7	1.4	0.1
ΣPMX	1.4	0.6	2.1		2.1	0.1	ΣPMX	1.9	0.7	1.5		2.0	0.1
OX	0.7	0.3	1.0	0.5		<0.1	OX	0.9	0.3	0.7	0.5		0.1
PM_{10}	15.6	6.5	22.6	10.8	22.5		PM_{10}	18.4	6.5	14.3	9.5	19.4	

These values show good agreement with those measured in other traffic polluted atmospheres in the UK, Scandinavia, and the US [Seila and Lonnerman, 1988; Sandroni et al., 1994; Bruckman et al., 1988; Field, 1994].

4.4.1.3 Correlational Statistics

Correlation matrices, which indicate the temporal relationship between the absolute concentrations of each aromatic hydrocarbon and PM_{10}, are presented for both sites in Table 4.4.

Table 4.4 Temporal Correlation Between the Concentrations of Individual Aromatic Hydrocarbon and PM_{10}

Fawcett Street

	Phase I						Phase II					
	B	Tol	EB	ΣPMX	OX	PM_{10}	B	Tol	EB	ΣPMX	OX	PM_{10}
B		0.967	0.930	0.860	0.961	0.186		0.441	0.434	0.556	0.385	-0.049
Tol			0.952	0.864	0.990	0.218			0.464	0.355	0.372	-0.088
EB				0.862	0.961	0.220				0.560	0.321	0.037
ΣPMX					0.849	0.509					0.658	0.241
OX						0.189						0.001

Holmeside Street

	Phase I						Phase II					
	B	Tol	EB	ΣPMX	OX	PM_{10}	B	Tol	EB	ΣPMX	OX	PM_{10}
B		0.894	0.630	0.709	0.812	0.493		0.924	0.294	0.887	0.303	0.662
Tol			0.790	0.846	0.935	0.349			0.926	0.183	0.734	0.734
EB				0.805	0.924	0.077				0.166	0.185	0.729
ΣPMX					0.868	0.417					0.701	-0.341
OX						0.285						-0.344

All presented values are correlation coefficients (r)

Generally, a poor correlation was found at each site between individual aromatic hydrocarbons and PM_{10}, suggesting their emission rates or source dependencies are dissimilar.

4.4.1.4 Frequency Distribution of BTEX Concentration Ratios

Chart 4.3 presents the frequency distribution of $[B/Tol]_{(0700\text{-}1800)}$, $[B/EB]_{(0700\text{-}1800)}$, $[B/\Sigma PMX]_{(0700\text{-}1800)}$ and $[B/OX]_{(0700\text{-}1800)}$ recorded at Fawcett Street during Phase I. For visual clarity, a two-period moving average of the category frequency's has been added to each plot (bold lines with data plotted as overlaying points).

Table 4.5 presents a statistical description of the frequency distributions of [BTEX] concentration ratios at both sites collected during both Phases.

Chart 4.3 Frequency Distribution of BTEX Concentration Ratios, Fawcett Street, Phase I

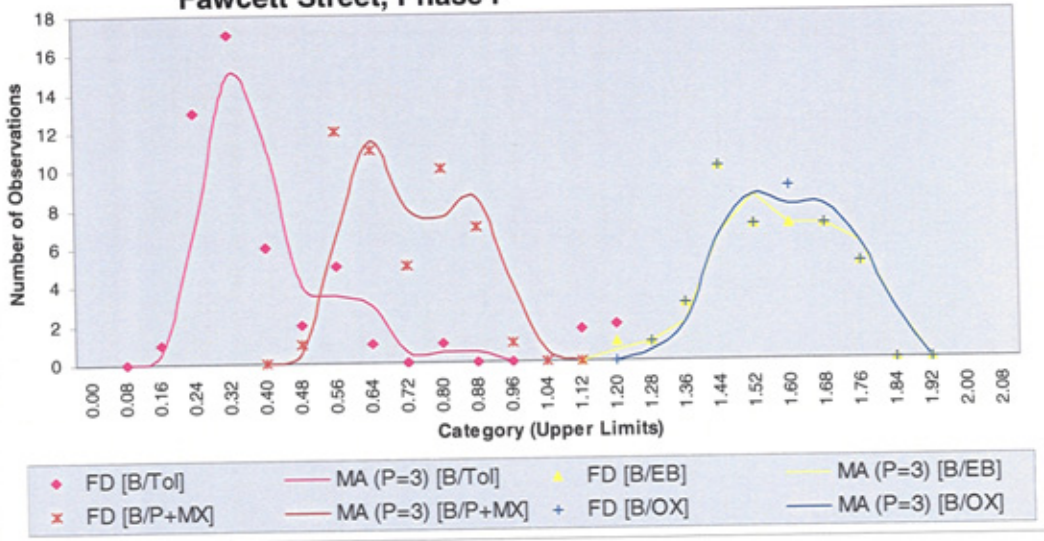


Table 4.5 Description of Frequency Distribution of [BTEX] Ratio Values

	Fawcett Street, Phase I				Fawcett Street, Phase II			
	[B/Tol]	[B/EB]	[B/ΣPMX]	[B/OX]	[B/Tol]	[B/EB]	[B/ΣPMX]	[B/OX]
Skew	1.28	0.70	0.41	0.44	1.48	0.21	NA [1]	NA [1]
Kurtosis	1.92	-1.02	-1.76	-0.93	0.35	-1.23	NA [1]	NA [1]
Mean±1σ	0.32±0.13	1.56±0.38	0.66±0.15	1.37±0.27	0.64±0.14	1.11±0.24	4.86±3.24	4.93±3.84
	Holmeside Street, Phase I				**Holmeside Street, Phase II**			
	[B/Tol]	[B/EB]	[B/ΣPMX]	[B/OX]	[B/Tol]	[B/EB]	[B/ΣPMX]	[B/OX]
Skew	1.05	0.46	0.49	0.47	1.00	0.13	0.65	0.96
Kurtosis	0.66	0.06	-1.40	-1.77	0.76	-0.91	-0.85	-0.93
Mean±1σ	0.42±0.04	1.58±0.30	0.73±0.17	1.48±0.18	0.36±0.06	0.51±0.10	0.80±0.33	1.10±0.47

[1] (NA) Too few measurements above detection limit were collected for a representative frequency distribution

The above table indicates that the 'shape' of each the frequency distributions for kerbside sites show reasonable agreement.

4.4.2 Rooftop Measurements

Statistical summaries of measurements of [SO_2], [NO_2] and [O_3] are presented in Table 4.6 below.

Table 4.6 Statistical Summary of Roof Top Measurements

	Fawcett Street					
	Phase I			Phase II		
	NO_2	O_3	SO_2	NO_2	O_3	SO_2
No. Results[1]	120	120	120	116	116	116
Mean (ppb)	58.0	27.8	33.5	75.1	58.1	22.7
Maximum (ppb)	97.8	50.6	131.1	115.1	85.3	53.8
	Holmeside Street					
	Phase I			Phase II		
	NO_2	O_3	SO_2	NO_2	O_3	SO_2
No. Results[1]	120	120	120	118	118	119
Mean (ppb)	63.1	33.0	33.8	70.8	44.4	22.7
Maximum (ppb)	103.9	55.9	128.1	110.1	74.7	53.8

[1] Above limits of detection

Correlation matrices for rooftop and ground-based measurements are presented below in Table 4.7.

Table 4.7 Temporal Intercorrelation Between Rooftop and Ground Based Measurements

Fawcett Street

	Phase I					Phase II				
	O_3	SO_2	B	Tol	PM_{10}	O_3	SO_2	B	Tol	PM_{10}
NO_2	-0.840	0.406	0.190	0.241	-0.062	-0.162	-0.131	-0.372	-0.095	-0.081
O_3		-0.446	-0.265	-0.282	0.137		-0.334	-0.545	-0.020	0.052
SO_2			-0.169	-0.308	-0.280			0.257	0.633	0.453

Holmeside Street

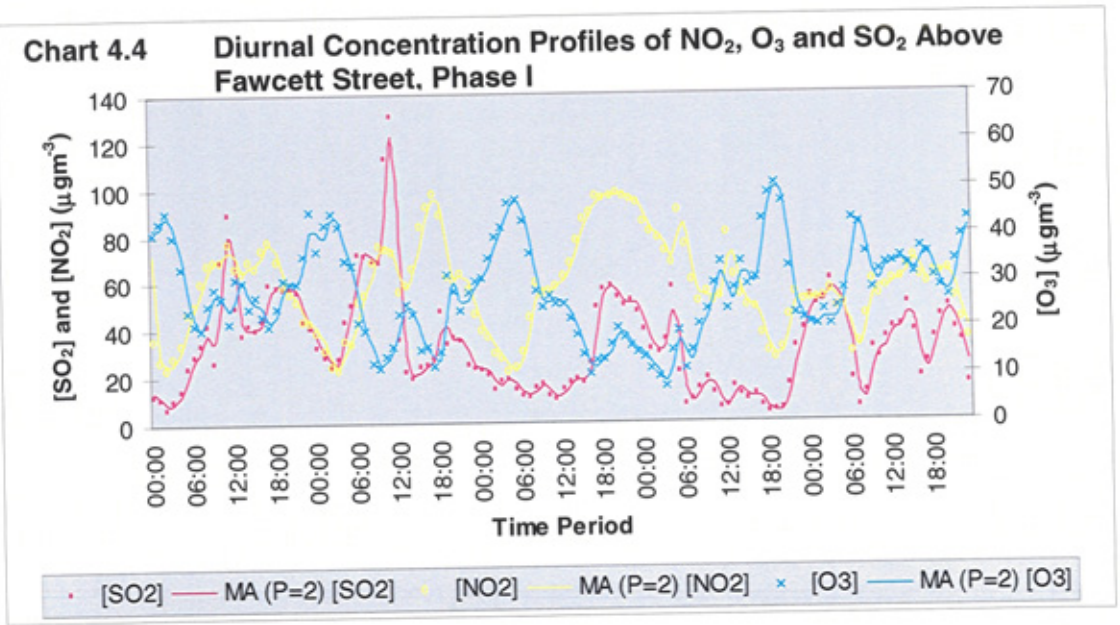
	Phase I					Phase II				
	O_3	SO_2	B	Tol	PM_{10}	O_3	SO_2	B	Tol	PM_{10}
NO_2	-0.793	0.385	0.570	0.648	0.385	-0.289	-0.131	0.873	0.936	0.602
O_3		-0.421	-0.314	-0.310	-0.244		-0.334	-0.413	0.108	0.049
SO_2			0.432	0.367	0.828			0.905	0.868	0.540

All values correlation coefficients (r) for day time measurement only

The table demonstrates poor correlation between roof-top and ground based measurements. A strong inverse correlation is also noted between NO_2 and O_3 within each of the measurement paths.

Chart 4.4 presents the diurnal concentration profiles of NO_2, O_3, and SO_2 above Fawcett Street. For visual clarity, a 2 period moving average has been plotted, with concentration values as overlaying data points.

Chart 4.4 Diurnal Concentration Profiles of NO_2, O_3 and SO_2 Above Fawcett Street, Phase I



The above chart illustrates the inverse relationship between the concentrations of O_3 and NO_2, whereas there appears to be a weak positive correlation between the concentrations of NO_2 and SO_2.

Charts 4.5, 4.6 and 4.7 present roof top data for $[NO_2]$, $[O_3]$ and $[SO_2]$ respectively.

Chart 4.5 Diurnal Profile of $[NO_2]$

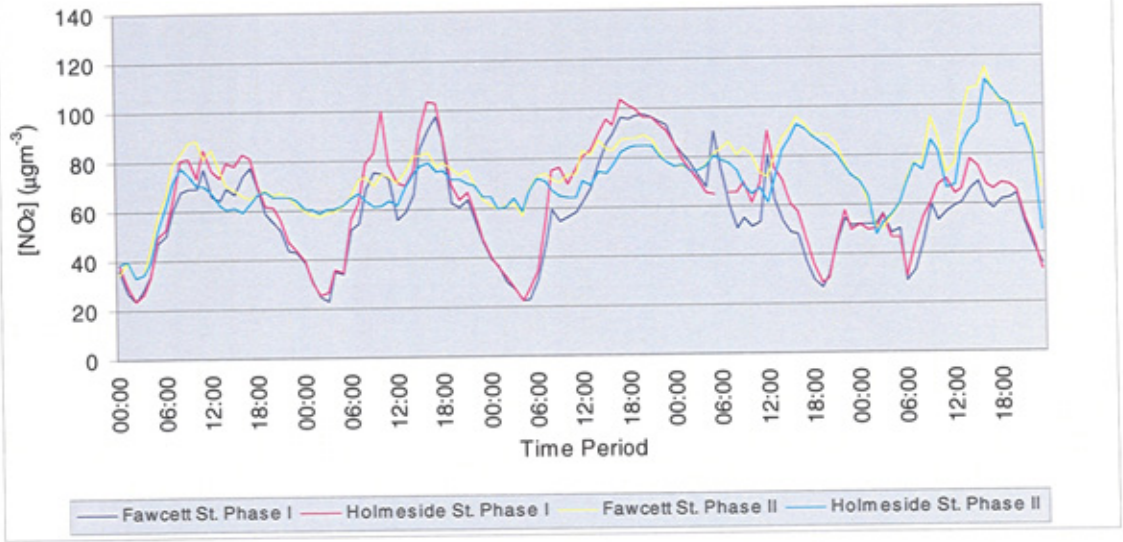


Chart 4.6 Diurnal Profile of $[O_3]$

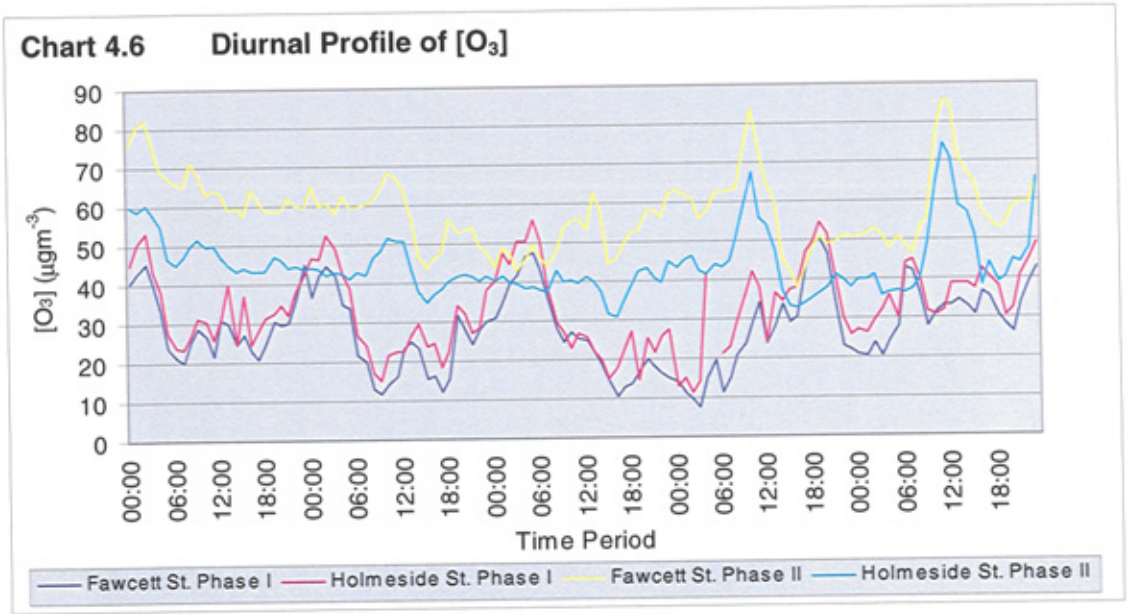
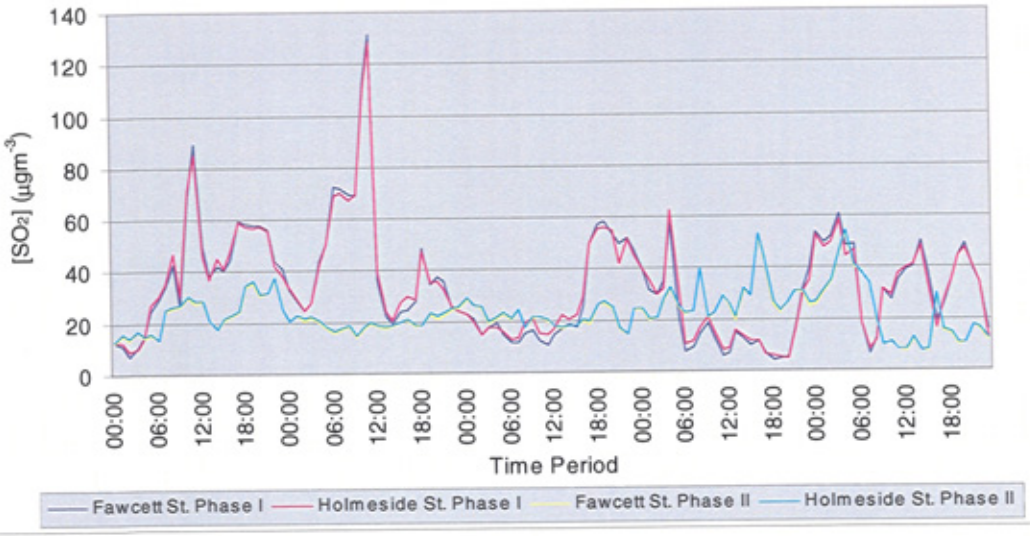


Chart 4.7 Diurnal Profile of [SO_2]



4.5 DISCUSSION

4.5.1 Kerbside Measurements

4.5.1.1 Statistical Features

Commonalties in the ranked order of BTEX noted for kerbside sites did not appear at Fawcett Street during Phase II (effectively an urban background site): (highest mean concentration first) toluene > benzene ≈ ethylbenzene> Σpara+metaxylene ≈ orthoxylene.

Significant deviation from the kerbside ranked order of mean [BTEX] within a sunlit, traffic polluted boundary layer environment, is likely to arise through photochemical ageing of urban air.

This proposition can be validated by comparison of:

- the rate constants (k_{OH}) of each aromatic hydrocarbon and the initial rates of reaction (J_0) of each BTEX aromatic with ·OH; and
- the mean proportion of each aromatic measured at their point of emission ($\alpha_{[BTEX]}$ Phase I), and the mean proportion of each aromatic at the urban background site ($\alpha_{[BTEX]}$ Phase II).

·OH - BTEX initial tropospheric reaction rates (J_0), calculated using values of k_{OH} and wintertime [·OH] noted in Section 2.3 (at 280.1K), are presented in Table 4.8 along with the differences between $\alpha_{[BTEX]\ Phase\ I}$ and $\alpha_{[BTEX]\ Phase\ II}$, at Fawcett Street.

Table 4.8 Relationship Between Kerbside and Urban Background $\alpha_{[BTEX]}$ and BTEX Boundary Layer Reactivity (Fawcett Street Data)

	$\alpha_{[BTEX]}$ [1] **Phase I**	$\alpha_{[BTEX]}$ [1] **Phase II**	$\frac{\alpha_{[BTEX]\ Phase\ I}}{\alpha_{[BTEX]\ Phase\ II}}$	Rate Constant [2] k_{OH} ($x10^{-12}$ cm^3 $molecule^{-1}s^{-1}$)	Init. Reaction Rate, J_o [6] ($x10^4$ molecules cm^{-3} s^{-1})
B	15.9	26.5	0.60	1.2 (3)	0.28
Tol	37.7	40.1	0.94	6.0 (3)	3.33
EB	10.5	22.2	0.47	7.1 (4)	1.08
ΣPMX	24.5	6.1	4.02	14.3 (3) / 24.8 (5)	7.07
OX	11.3	5.1	2.22	13.0 (3)	2.18

[1] Mean proportion, or $\alpha[BTEX] = \left(\frac{\bar{x}[BTEX]}{\bar{x}\Sigma[BTEX]}\right)x100$ [2] At 298K, see Table 2.6

[3] Devolder, 1994 [4] Simpson, 1995 [5] Prinn et al., 1994

[6] Initial reaction rate calculated using the second order rate law :

$$\frac{-d[BTEX]}{dt} = K_{OH}[OH] * [BTEX]$$

Where: [OH] = $0.02x10^6$ molecules cm^{-1} (modelled wintertime [·OH] [Crutzen and Gidel, 1983]);

[BTEX] calculated from Phase I Fawcett Street $\bar{X}_{[BTEX]}$, at the recorded average daytime temperature of 280.1K; and

An averaged value of k_{OH} for para and metaxylene has been applied (which assumes each isomer constitutes 50% of the measured ΣPMX).

Least squares linear regression of ($\alpha[BTEX]_{Phase\ 1}$ /$\alpha[BTEX]_{Phase\ 2}$) vs. k_{OH} for each BTEX aromatic is presented below in Chart 4.8.

Chart 4.8 Relationship Between α[BTEX] and k_{OH} for Kerbside and Urban Background Sites

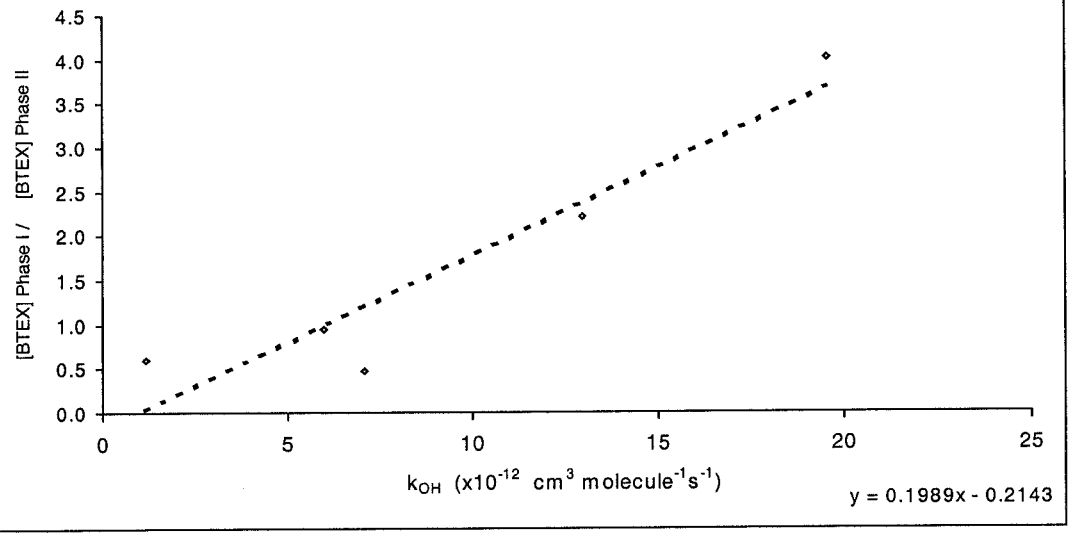


Chart 4.8 demonstrates a positive, strong correlation between (α[BTEX] $_{Phase\ 1}$ / α[BTEX] $_{Phase\ 2}$) and k_{OH} (r=+0.94). The initial rates of reaction with ·OH demonstrate similar agreement with (α[BTEX] $_{Phase\ 1}$ / α[BTEX] $_{Phase\ 2}$) (r=+0.89), suggesting that the difference between kerbside and urban background ranked order of mean [BTEX] can be accounted for through photochemically aged air being sampled at the urban background site. This feature has only become apparent at a site some distance from a significant source of 'non-aged' BTEX aromatics.

These findings cannot be adopted as a confident indicator of photochemical potential of a boundary layer environment, or the age of a sampled air parcel. This is because the degree of mixing between photochemically aged and 'un aged' parcels of air is not known and highly variable within turbulent city centre environments.

4.5.1.2 BTEX Concentration Ratios

Ratios of individual mean [BTEX] values at each kerbside site (presented in Table 4.3) broadly agree with the limited number of published values for the UK [Barrefors, 1996].

Total mean concentration ratios calculated from the UK Government's Automatic Urban Network (AUN) of remote monitoring sites are presented in Table 4.9. The AUN sites chosen for comparison (upon the basis of their proximity to Sunderland), are described briefly in Appendix 1.

Table 4.9 Total Mean [BTEX] Concentration Ratios for Sunderland, Leeds and Middlesbrough City Centres

Ratio	Sunderland [1]		Middlesborough	Leeds
	Kerbside (Fawcett Street)	Urban Background (Fawcett Street)	Urban Industrial	Urban Background
$\bar{X}$ [B/Tol]$_{(0700\text{-}1800)}$	0.4	0.7	0.2	0.4
$\bar{X}$ [B/EB]$_{(0700\text{-}1800)}$	1.5	1.2	NA	2.8
$\bar{X}$ [B/ΣPMX]$_{(0700\text{-}1800)}$	0.6	4.5	0.4	0.6
$\bar{X}$ [B/OX]$_{(0700\text{-}1800)}$	1.4	5.2	1.0	2.0

[1] Phase I data
All concentration ratios have been calculated over matching time periods.

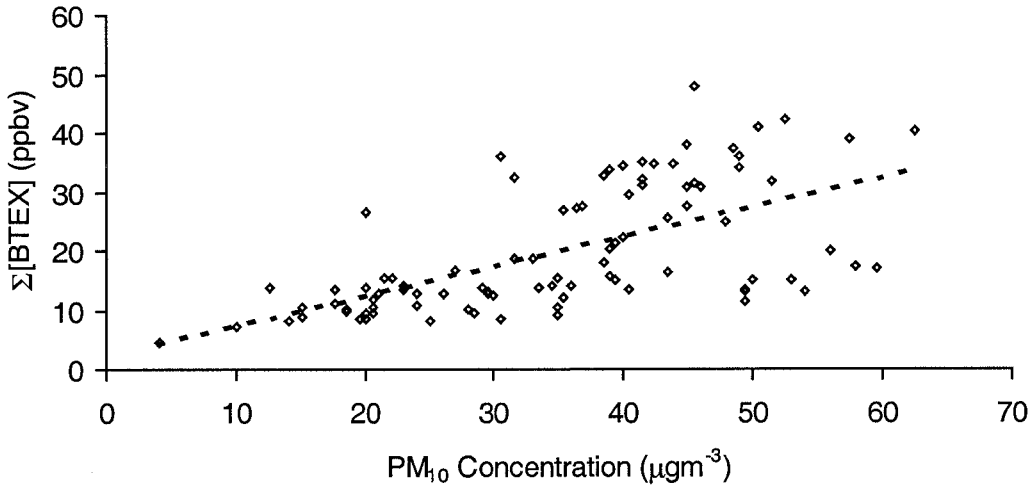
Table 4.9 demonstrates a range of ratio values for a number of locality types, and generally shows a lack in spatial coherency in ratios measured at sites of different 'class'. Reasonable agreement, however, appears across each of the sites for mean $[B/Tol]_{(0700\text{-}1800)}$ which may be linked to benzene and toluene demonstrating the longest tropospheric lifetimes of the BTEX aromatics.

4.5.1.3 Correlational Statistics

A salient feature of [BTEX] kerbside measurements is their remarkable temporal intercorrelation. Each BTEX aromatic generally demonstrates a strong, positive correlation with other BTEX aromatics at both of the ground-based measurement sites during Phase I, and Holmeside Street during Phase II. This feature can be interpreted as the BTEX having a single significant source within the locality of each kerbside site, and agrees with suggestions from earlier studies that mean concentration ratios of individual BTEX aromatics remain approximately constant near to road traffic [Wathne, 1983].

Although Chart 4.2 indicates reasonable, positive temporal correlation between Σ[BTEX] and $[PM_{10}]$ for kerbside measurements, the magnitude of this correlation is considerably lower than coefficients calculated between individual BTEX aromatics. This point is made clearer in the scatter plot of all data collected at kerbside sites (Chart 4.9).

Chart 4.9 Scatter Plot of Σ[BTEX] and [PM_{10}], Kerbside Data



The intercept at the Y axis (2.77μgm^{-3}) indicates that PM_{10} and BTEX aromatics demonstrate a common source dependence at kerbside sites. Given the number of sources of particulate matter in an urban environment this feature is surprising.

4.5.1.4 Frequency Distribution

Chart 4.3 and Table 4.5 implies that ratios of individual BTEX close to intense road traffic do not undergo significant systematic variation during daytime hours.

Kurtosis values for each ratio distribution again show reasonable agreement between kerbside sites. However, they do demonstrate a wide range of values amongst individual measurements. The 'broadness' of a distribution can be attributed principally to two factors:

- the cumulative measurement precision of the two determinants from which a ratio value has been calculated; and
- the degree of random variation in the source term.

The measurement precision, in terms of the 95% confidence interval, of BTEX aromatic ratios is as follows (Section 3.1):

B/Tol = 3.0% B/EB = 3.6% B/ΣPMX = 5.6% B/OX = 3.8%

Therefore the degree of variability of aromatics within road traffic emissions recorded at the kerbside sites (Table 4.5) is as follows (which assumes that other sources of BTEX were not significant at these sites):

B/Tol = 11.8% B/EB = 17.2% B/ΣPMX = 22.8% B/OX = 21.0%

The above values, indicate that emissions of BTEX from UK road traffic occur with a high degree of proportional consistency, particularly for B/Tol, and this feature of traffic emitted aromatics hydrocarbons will become important in the following chapter. It is surprising, however, that such proportional consistency exists, when variables dictating the rate of emission from road traffic are considered, such as fuel compositional variability, vehicle age and driving patterns.

4.5.2 Rooftop Measurements

4.5.2.1 Concentration Profiles of Roof Top Measurements

Chart 4.4 demonstrates a number of features:

- a distinct inverse correlation between $[O_3]$ and $[NO_2]$, with daytime peaks of $[NO_2]$ and night time peaks of $[O_3]$ (discussed below);
- $[O_3]$ and $[NO_2]$ demonstrate diurnal seasonality
- $[SO_2]$ does not demonstrate diurnal seasonality, and shows little correlation between $[O_3]$ or $[NO_2]$; and
- $[SO_2]$ peaks occur both during daytime and night time periods.

The latter two features are to be expected, as there are generally few sources of SO_2 within urban areas of the UK. Road traffic does not constitute a significant source of SO_2, as the sulphur content of diesel fuel is relatively small (~0.04%) and sulphur content of petrol fuel insignificant [Quality of Urban Air Review Group, 1994]. The

principle sources of SO_2 in the UK are (1998 estimates): power generation (66%) and industry (12%), with road transport constituting a small fraction (1%) [National Atmospheric Emissions Inventory, 1998]. At the time of writing of this document, a major local source of SO_2 to the district of Tyne and Wear was Blyth Power Station, which operated on coal and heavy fuel oil. However, examination of local wind directions during periods of high [SO_2] (accounting for time of flight of an SO_2 bearing plume from the power station stacks) suggested that SO_2 arrived to the study sites from other source/s.

Charts 4.5, 4.6 and 4.7 demonstrate:

- that very little spatial variation in the concentration of SO_2 exists between DOAS paths, indicating the sample atmosphere of both DOAS paths are homogenous with respect to SO_2 and confirms the absence of significant localised emission sources;
- that [NO_2] demonstrates slight spatial variation, however is highly temporally correlated between individual sample atmospheres of the DOAS paths; and
- ozone demonstrates the greatest degree of spatial variation, however again is highly temporally correlated between DOAS paths.

4.5.2.2 Correlational Features

Table 4.7 indicates a lack of correlation between roof top and ground based measurements.

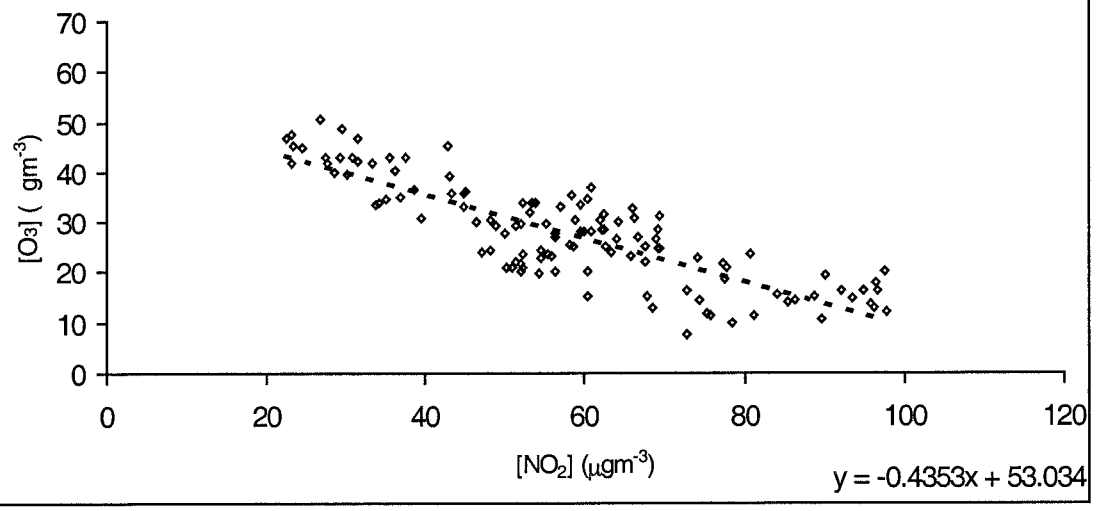
It would not be expected that a direct temporal correlation would exist between BTEX (which are primary pollutants) and ozone (a secondary pollutant, the formation of which is augmented by emission of hydrocarbons). Similarly, as SO_2 has not demonstrated seasonality in diurnal or daytime concentration profiles, correlation would not be expected with BTEX which are emitted at regular periods of the daily cycle.

The open path nature of DOAS provides spatially representative measurements for a relatively large volume of the boundary layer, whereas ground-based measurements are effected more significantly by local fluctuations in source emission strengths. In addition, the extent of vertical mixing of primary pollutants within the street canyons is not likely to be extensive where lateral wind movements are high, and residence time of pollutants within the street canyons are therefore low.

4.5.2.3 Boundary Layer Photochemistry

Chart 4.10 demonstrates the coherency of the inverse correlation between ozone and NO_2.

Chart 4.10 Scatter Plot of $[O_3]$ and $[NO_2]$, Phase I, Fawcett Street



The primary emission source of oxides of nitrogen within urban areas is road traffic (estimated 46% for the UK in 1998 [National Air Quality Information Archive, 1998]), of which the monoxide constitutes an estimated 85-90% from combustion sources [Quality of Urban Air Review Group, 1994].

The net photochemical loss of ozone verses the net photochemical formation of ozone depends upon the concentration nitric oxide. In the absence of emission of VOCs, ozone undergoes the following reactions [Atkinson, 2000]:

$NO_2 + h\upsilon \longrightarrow NO + O(3P)$ R4.1

$O(3P) + O_2 + M \longrightarrow O_3 + M$ R4.2

Where M = O_2 or N_2

However because O_3 reacts rapidly with NO:

$NO + O_3 \longrightarrow NO_2 + O_2$ R4.3

Reactions R4.1-R4.3 result in photoequilibrium between NO, NO_2, and ozone, however in the presence of VOCs (such as those associated with road traffic emissions) this balance is perturbed through the formation of RO_2 and HO_2 free radical species (Table 2.4):

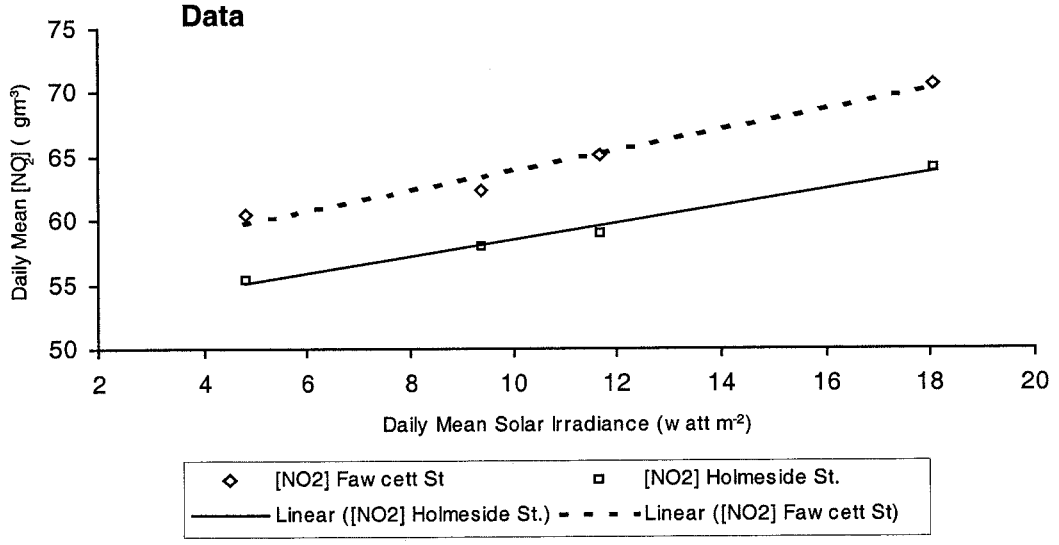
$HO_2 + NO \longrightarrow \cdot OH + NO_2$ R4.4

$RO_2 + NO \longrightarrow RO + NO_2$ R4.5

Therefore the extent of conversion of NO to NO_2 within an urban atmosphere depends upon the concentration of ozone, alkoxy and hydroperoxyl radicals, species which are related to the steady state [·OH]. As discussed in Section 2.3, OH radicals are formed (predominately so) through the short wave photolysis of ozone, and so are generated to steady state concentrations dictated by the prevailing solar flux and availability of ozone [Atkinson 2000].

This is evident within the collected data: regression of daily averages of NO_2 with daily average solar flux demonstrates a positive linear relationship with similar slopes for both sites during Phase I (r=+0.87, Fawcett Street; +0.85 for Holmeside Street; r=+0.99 and +0.97 respectively with the omission of one outlier). This feature is presented for Fawcett Street (both DOAS paths) in Chart 4.11 below. Solar irradiance data was provided by the University of Northumbria, recorded concurrently to Phase I and II measurements at the Northumberland Building, Newcastle City Centre.

Chart 4.11 Relationship Between [NO_2] and Solar Irradiance, Phase I Data



This relationship suggests that where the daily rate and duration of emission of NO and VOCs remains approximately constant, daily mean solar flux alone provides a reasonable gauge of photochemical activity of a traffic polluted boundary layer environment.

4.5.2.4 Significance of the Traffic Management Scheme

Clear reduction in [BTEX] and [PM_{10}] is demonstrated throughout daytime periods at Fawcett Street following the implementation of the traffic management scheme. It is, however, important to recognise the critical role of meteorology in the dispersive capacity of a boundary layer environment, and in the transport of pollutants from other road sources to the study sites (Table 4.10).

Table 4.10 Meteorological Conditions, Phase I and Phase II, Fawcett Street				
	Wind Speed [1] (ms^{-1})	Primary Wind Vector (degrees)	Secondary Wind Vector (degrees)	Boundary Layer Height [2] (m)
Phase I	4.4	270-315 (62%)	45-90 (22%)	667 (n=57)
Phase II	5.1	270-315 (55%)	45-90 (45%)	1011 (n=58)

[1] Recorded at ground level

[2] Calculated from wind speed and atmospheric stability class (Pasquil Gifford) estimates for Newcastle upon Tyne (The Met Office)

Mean wind speeds and wind directions at the site, and of the local weather system, demonstrate consistency between Phase I and Phase II study periods (Table 4.10). Mean boundary layer height is noted to differ between study Phases, however it is likely that this feature would only significantly affect measurements collected some distance from the source, or those collected over a considerable length of time.

Table 4.11 summarises the changes in absolute concentrations of each pollutant resulting from the traffic management scheme.

Table 4.11 Results of Traffic Management Scheme									
Site	B	Tol	EB	ΣPMX	OX	PM_{10}	NO_2	O_3	SO_2
Fawcett Street (% Change)	-66	-79	-59	-96	-91	-64	+23	+52	-32
Holmeside Street (%Change)	0	+6	+6	-22	-20	-32	+11	+25	-32

The above table demonstrates the reduction in absolute concentration of BTEX, which, with consideration of the lack of significant change noted at Holmeside Street, is likely to be attributable to the reduction in road traffic volume.

It is interesting to note that $[O_3]$ and $[NO_2]$ measurements did not demonstrate a comparable reduction along Path 1 (Fawcett Street) as a result of the scheme. As both O_3 and NO_2 are formed throughout the depth of the sunlit boundary layer, it is reasonable to adopt rooftop concentrations as indicators of the corresponding ground

level concentration of each species. Upon this basis, although the traffic management scheme has brought about considerable reduction in public exposure to BTEX and PM_{10}, exposure to O_3 and secondary NO_2 appears to have remained largely unchanged.

4.5.2.5 Presentation and Publication

The concurrent measurement of a number of tropospheric gases and PM_{10} formed the focus of a paper presented to the Trabzon International Energy and Environment Symposium (TIEES), Trabzon, North Turkey. The paper, published in the Proceedings of TIEES 1998, is presented in Appendix 6.

4.6 CONCLUSIONS

The Sunderland City Centre study has indicated a number of important features:

- that near to road traffic, proportional concentrations of BTEX aromatics demonstrate a very high degree of temporal consistency;
- at an urban background site, dissimilar proportional BTEX concentrations were noted. Upon the basis of the experimental data, it has been suggested that differential oxidation of [BTEX] may account for such differences between urban background and kerbside [BTEX] ratio values;
- upon the basis of conversion of NO to NO_2, sunlight has been shown to be an effective indicator of the oxidative capacity of a traffic-polluted atmosphere; and
- that public exposure to secondary pollutants may not necessarily be reduced through traffic management on a small scale. However traffic management has been shown to be beneficial in the reduction of ground level exposure to [BTEX], and most likely other traffic generated primary pollutants such as CO, NO_2, PM_{10}, and 1,3-butadiene.

The next chapter furthers this study by consideration of BTEX concentration ratios over the complete daily cycle, in order that the nocturnal behaviour is explored.

5 BEHAVIOUR OF BTEX IN THE FREE BOUNDARY LAYER

5.1 INTRODUCTION

Relatively few studies have considered ratios of individual aromatic hydrocarbons as a means of exploring their boundary layer behaviour. A number of authors, however, have recognised that BTEX concentration ratio's (averaged over hours to days) may be used for source apportionment or determination of the age of a parcel of polluted air in particular environments [Rappenglück and Fabian, 1998; Wathne, 1983; Field et al., 1992]. The previous chapter demonstrated that individual [BTEX] ratios near to intense road traffic occur with a high degree of temporal consistency. However, because the BTEX aromatics exhibit differing reactivity to $\cdot OH$ and $NO_3\cdot$ radicals (Section 2.3), and collectively demonstrate a range of Henry's Law constants, gas phase diffusion coefficients and boiling points (Appendix 3), it is likely that temporal differentiation of the concentrations of individual BTEX aromatic ratio's will occur daily.

This chapter explores diurnal features of aggregated ratios of [BTEX] values collected at a single ground based site in Newcastle City Centre, over a period of six weeks. The study was carried out during wintertime, in order that oxidative transformation of BTEX aromatics was minimised (low solar flux) and other postulated sink mechanisms maximised (see Table 2.9).

This study has been complimented by an earlier, shorter investigation conducted in Whitehaven, Cumbria, where road traffic density within the town centre was significantly lower than Newcastle upon Tyne. This second site was chosen to corroborate the findings of the Newcastle City Centre (NCC) Study.

5.2 MEASUREMENT DETAILS

The study sites are described in detail below, however, a summary of data collection is provided in Table 5.1.

Table 5.1 Summary of Study Sites

Site Name	Locality Description [1]	Measurement Dates	n[BTEX] / Cap (%) [2]	Other Measurements [3]
Northumberland Street, Newcastle upon Tyne	Roadside, Urban	20.11.97 – 04.01.98	1545 / 91	WS, WD, AT, PM_{10}, SF[4], RF[5], RTF[6]
Whitehaven town Centre, Cumbria	Suburban, background	04.03.96 – 28.3.96	701 / 89	WS, WD

[1] See Appendix 2 for locality definitions

[2] Mean number of half hourly [BTEX] measurements / mean data capture for BTEX. Individual data capture for individual BTEX is presented in Table 5.2

[3] WS =Wind Speed; WD =Wind Direction, AT = Air Temperature, SF = Solar Flux; RF = Rainfall; RTF =Road Traffic Flow

[4] SF measurements collected by The University of Northumbria, Newcastle upon Tyne

[5] RF measurements collected by The Met. Office, Newcastle upon Tyne

[6] RTF measurements provided by the Division of PHEP, Newcastle City Council. Values presented in this chapter have been derived from manual traffic counts and factored using Global factors for Newcastle upon Tyne city centre

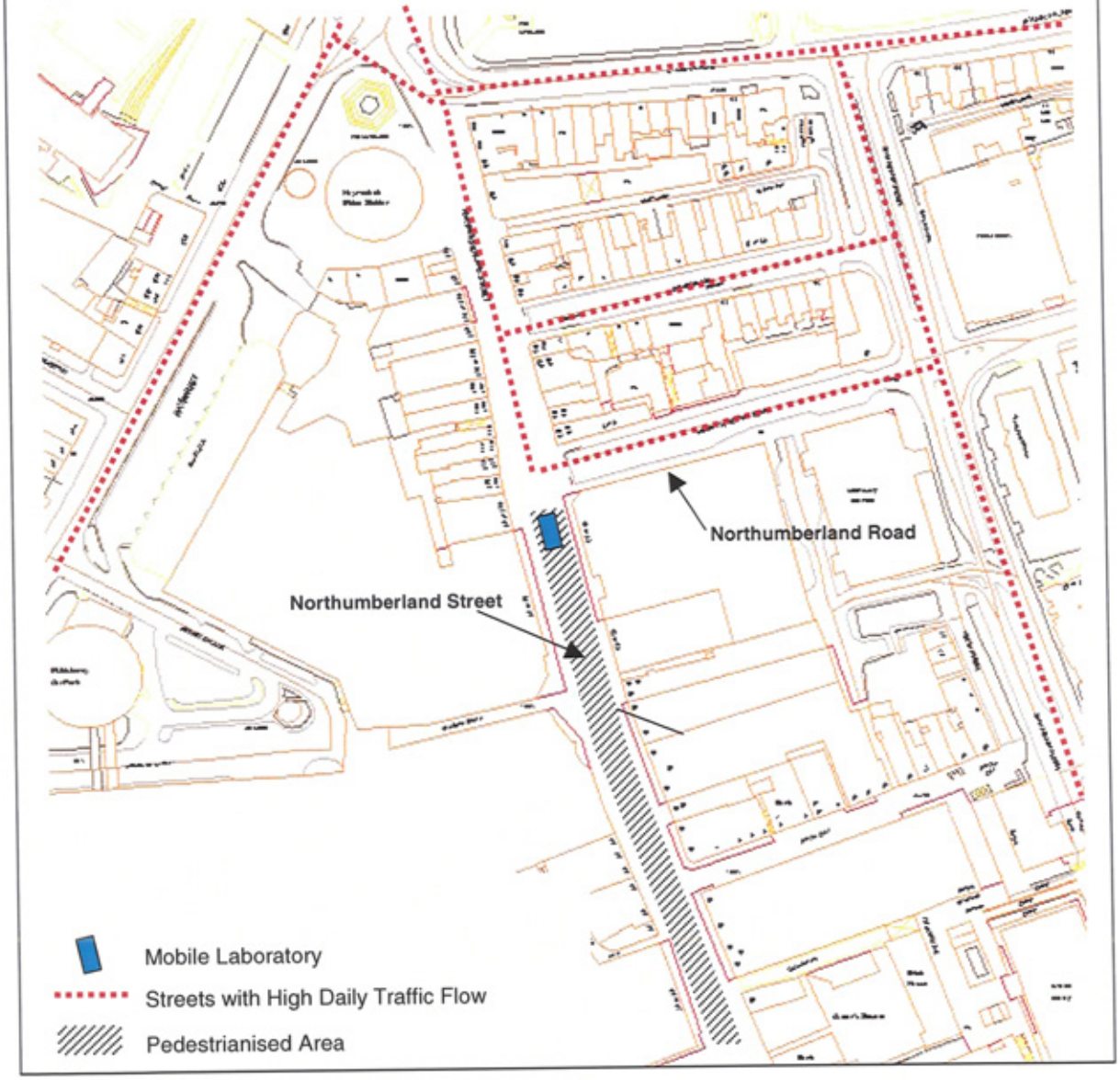
5.2.1 Northumberland Street, Newcastle City Centre, Tyne and Wear

The city of Newcastle upon Tyne is located 8 miles from the north east coast of England. At the time of this study, the city centre received a high daily flow of road traffic, which represented the principal source of BTEX aromatics near to the study site (fuel stations and industry were not likely to be significant at the chosen study location).

The ML was located 4m from Northumberland Road, a relatively minor inner city road which, at the time of the study, conveyed an average 284 vehicles per hour between 0600hrs – 2200hrs, and an average of 37 vehicle per hour between 2200-0500hrs [source – Newcastle City Council]. Northumberland Street is situated to the north of

the city centre. Figure 5.1 shows the location of the ML, Northumberland Road and other significant road sources near to the measurement site.

Figure 5.1 Northumberland Street Site, Newcastle upon Tyne



Operation and calibration of the TD-GC-FID and TEOM instruments was as described in Chapter 3. Nine consecutive days of data were lost through vandalism of the ML.

Measurement of atmospheric temperature, wind speed, and wind direction were performed concurrently to measurements of [BTEX] and [PM_{10}] at the study site.

Additional measurements were provided by third parties (detailed in Table 3.3), which comprised hourly solar irradiance and rainfall measurements in Newcastle upon Tyne, and a manual hourly traffic flow count at Northumberland Road.

5.2.2 Church Street, Whitehaven Town Centre, Cumbria

Whitehaven (Cumbria) is a relatively small town located on the north west coast of England. The town centre received significant road traffic during daytime hours only, and was not located next to major industrial developments, or cities (the nearest city being Carlisle, 44km north east).

The mobile laboratory was located within a car park approximately 13 metres from Church Street, which constituted part of the ring road, which encircled the town centre.

The car park was small (spaces for 20 cars), and used infrequently after 6pm, however Church Street, at the time of the study, conveyed an average 160 vehicles per hour between 0600hrs – 2200hrs, and an average of 15 vehicle per hour between 2200-0500hrs [source - Copeland Borough Council].

Monitoring began on the 28th February 1996, and ended on the 4th of April 1996.

5.3 RESULTS

5.3.1 Descriptive Statistics

5.3.1.1 Statistical Features of [BTEX] and [PM_{10}]

A statistical summary of ground based measurements is presented in Table 5.2 below.

Table 5.2 Statistical Summary of Ground-Based Measurements

Parameter	B	Tol	EB	ΣPMX	OX	PM_{10}
Northumberland Street, Newcastle City Centre						
No. Results (n) / Cap (%)[1]	1334 / 88	1464 / 97	1497 / 99	1500 / 99	1380 / 91	1380 / 91
Mean (ppb, or μgm^{-3} for PM_{10})	1.2	2.8	0.7	1.8	0.8	21.0
Mean Proportion[2] (%)	15.1	37.4	11.0	25.2	11.3	NA
Maximum (ppb, or μgm^{-3} for PM_{10})	11.1	26.3	6.4	15.6	7.1	74.5
Church Street, Whitehaven Town Centre						
No. Results (n) / Cap (%)[1]	608 / 87	618 / 88	632 / 90	621 / 89	641 / 92	
Mean (ppb, or μgm^{-3} for PM_{10})	1.6	3.5	1.1	0.6	0.9	
Mean Proportion[2] (%)	20.4	45.0	14.9	7.7	12.1	
Maximum (ppb, or μgm^{-3} for PM_{10})	11.7	26.6	9.2	16.9	8.4	

[1] Number of measurements above limit of detection / % data capture

[2] Mean proportion of the total BTEX concentration, or $\alpha[BTEX] = \left(\frac{\bar{x}[BTEX]}{\bar{x}\Sigma[BTEX]} \right) x100$

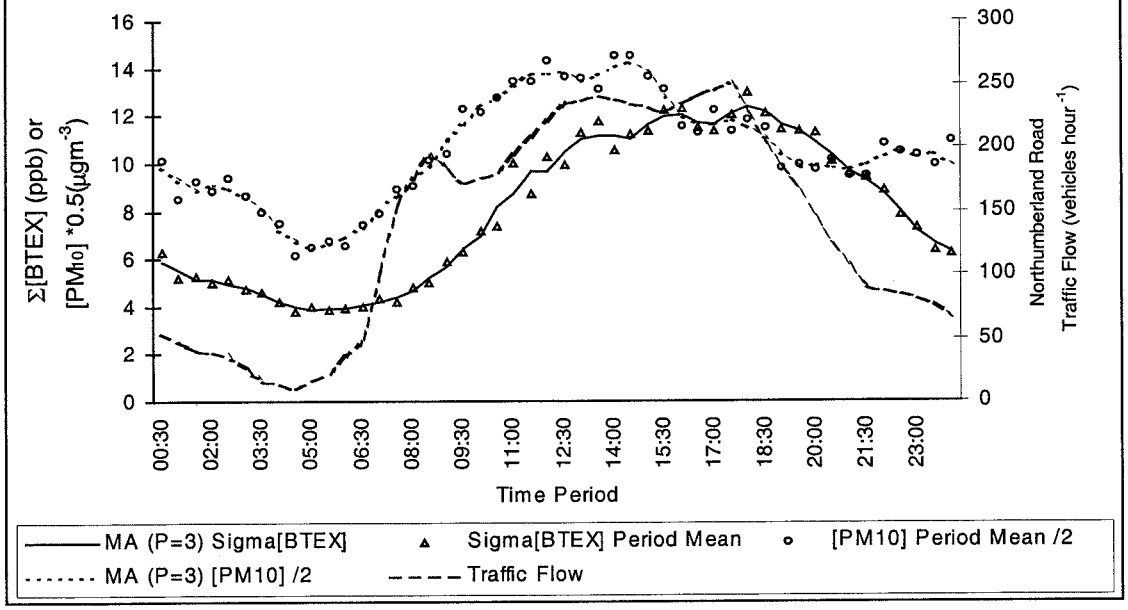
With the exception of Σ[PMX], the proportions of BTEX demonstrate reasonable agreement between the study sites. This suggests that [BTEX] at both sites had a common, compositionally similar, emission source. It is interesting, and perhaps unexpected, that the city centre site demonstrates on average, lower absolute concentrations of BTEX aromatics than the suburban site. This illustrates the difficulties associated with exploring measurements of absolute concentrations of an

atmospheric trace species, where the degree of mixing of the boundary layer is unknown, and hence an atmospheric sample may not be representative of the pollution load at that locality.

Chart 5.1 graphically presents mean aggregated [PM_{10}] and Σ[BTEX] for each 30 minute period of all study days. A 3-period moving average (noted as [MA (P=3)] in Chart 5.1) has been included over both plots for visual clarity.

Estimated hourly traffic flow for Northumberland Road is also included.

Chart 5.1 Period Mean [PM_{10}] and Σ[BTEX], Northumberland Street Site



The above chart illustrates a characteristic diurnal trend of primary pollutants throughout the daily cycle, suggesting a positive correlation between [BTEX] and [PM_{10}] with road traffic flow. However, it appears that Σ[BTEX] reaches its maximum concentration during the daily cycle several hours after the maximum is reached by PM_{10}.

5.3.1.2 Correlational Statistics

Table 5.3 presents the intercorrelation between the concentration of individual BTEX aromatics, and PM_{10}.

Table 5.3 [BTEX] and [PM_{10}] Correlation Matrix

	Northumberland Street					Whitehaven Town Centre				
	Tol	EB	ΣPMX	OX	PM_{10}		Tol	EB	ΣPMX	OX
B	0.938	0.921	0.919	0.936	0.177	**B**	0.769	0.524	0.598	0.526
Tol		0.927	0.941	0.950	0.195	**Tol**		0.461	0.530	0.501
EB			0.914	0.919	0.144	**EB**			0.822	0.812
ΣPMX				0.888	0.123	**ΣPMX**				0.888
OX					0.104	**OX**				

Corroborating findings of the previous chapter, measurements of BTEX aromatics collected near to road traffic (Northumberland Street site) demonstrate a strong positive intercorrelation. Measurements collected in Whitehaven town centre, some distance from a relatively minor road source, demonstrate poor-reasonable positive intercorrelation. It is interesting to note that BTEX concentrations at the city centre site show little correlation with [PM_{10}], again suggesting differing emission rates.

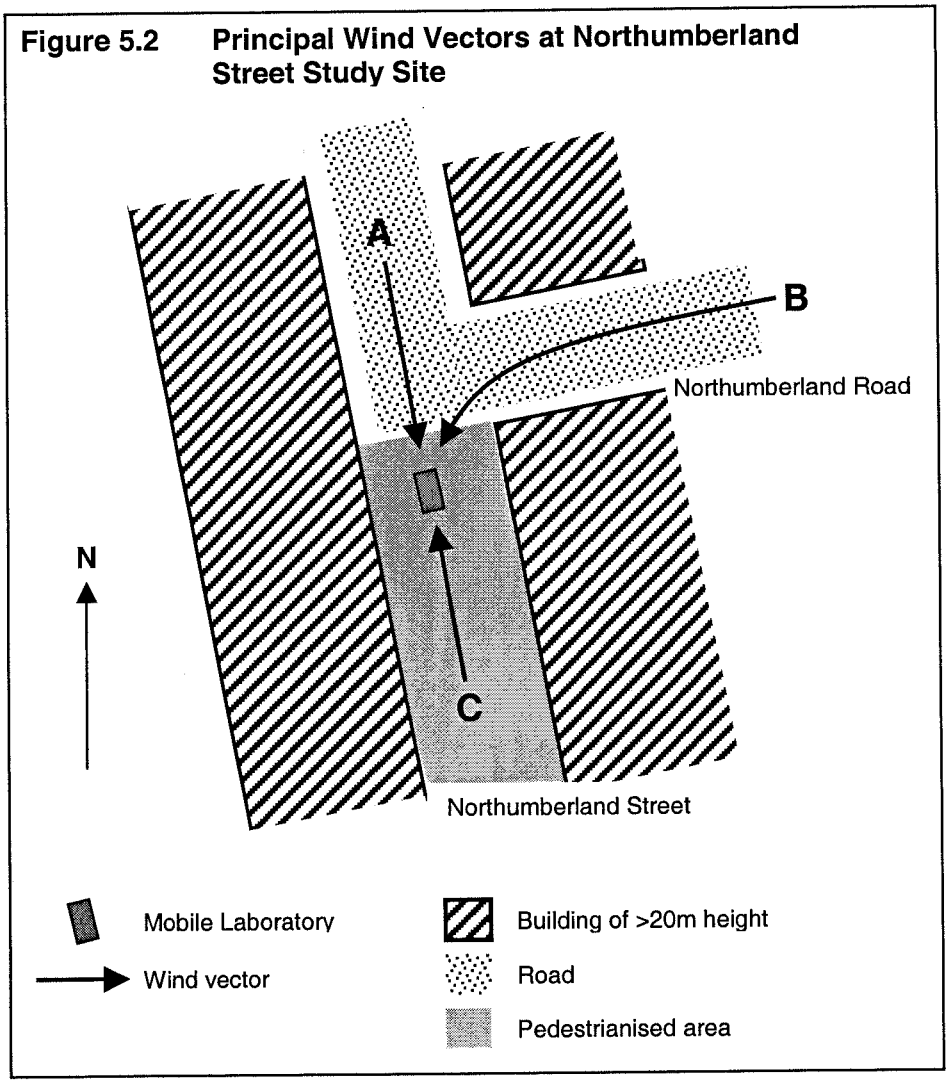
5.3.2 Statistical Analysis of Individual BTEX Aromatic Concentration Ratios

Aggregated ratios of diurnal [BTEX] measurements have been calculated and are presented on the following pages as a *net* time series over the study periods (using the procedure described in Chapter 3). Initially, however, the significance of wind transport is presented.

5.3.3 Wind Transport Vectors at the Northumberland Street Site

Measurements of wind direction indicated that sampled air arrived at the study site from one of three 'vector categories' dictated by the orientation of the street canyons at the study locality (as indicated in Figure 5.2).

Figure 5.2 Principal Wind Vectors at Northumberland Street Study Site



The vector categories represent a range of wind directions (0° is magnetic north):

- Vector A comprises half-hourly mean wind directions of 270°-0°
- Vector B comprises half-hourly mean wind directions of 1°-70°
- Vector C comprises half-hourly mean wind directions of 71°-269°

Vectors A and B originate from street canyons within 10m of the study site, which accommodate road traffic. The nearest road source along vector C is the intersection between Northumberland Street, and Blackett Street approximately 300 metres south-south-east from the study site.

Table 5.4 presents primary and secondary wind vectors for each study day recorded at the measurement site. Vectors are presented for day time (0630-2200) and night time (2230-0600) periods.

Table 5.4 Wind Vectors Arriving at the Northumberland Street Study Site

Primary / Secondary Wind Vector	Daytime (0630-2200)	Night Time (2230-0600)[1]
A	20-24.11.97; 20-24.12.97	21-23.12.97; 29.12.97
A/B		23.11.97; 24.12.97
A/C	25.12.97; 28.12.97	
B		22.11.97; 24-25.11.97; 25.12.97
C	11.12.97; 13-19.12.97; 26-27.12.97; 01-02.01.98	15-19.12.97; 26-27.12.97
C/A	12.12.97; 29.12.97	20.12.97; 28.12.97; 20.12.97

[1] Night time date refers to period after midnight

Measurements indicate that vectors A and C predominate during daytime hours, whereas night time vectors include significant wind movement along Northumberland Road (vector B).

5.3.3.1 Significance of Transport Vectors

Aggregated BTEX concentration ratios for day time and night time transport vectors are presented in Table 5.5 below. Study days that have demonstrated primary wind

vectors A and B are presented collectively, as both are associated with the conveyance of emissions from road traffic using Northumberland Road to the study site.

Table 5.5 BTEX Aromatic Concentration Ratios for Primary Wind Vectors				
Ratio [1]	Day time (0630-2200)		Night time (2230-0600)	
	Vector A	Vector C	Vector A+B	Vector C
$\bar{X}$ [B/Tol]	0.35	0.44	0.39	0.46
$\bar{X}$ [B/EB]	1.21	1.80	1.20	1.54
$\bar{X}$ [B/ΣPMX]	0.52	0.72	0.54	0.67
$\bar{X}$ [B/OX]	1.15	1.64	1.31	1.53
$\bar{X}$ Σ[BTEX]	11.25	17.45	6.43	8.31
[1] Mean ratio covering the entire study				

Table 5.5 indicates an apparent systematic difference between wind vectors in terms of BTEX concentration ratios, particularly for [B/EB]. In addition, the mean Σ[BTEX] for the study appeared greater for vector C, even though the nearest significant road source along this direction was approximately 300m from the site.

5.3.3.2 Frequency Distribution of [BTEX] Ratios

Table 5.6 presents normality tests, kurtosis and skewness distribution shape parameters for individual [BTEX] ratios. Analysis using kurtosis and skewness tools indicated that individual BTEX concentration ratios are not log-normally distributed.

Table 5.6 Statistical Summary of [B/Tol]$_{(TOTAL)}$, [B/EB]$_{(TOTAL)}$, [B/ΣPMX]$_{(TOTAL)}$, and [B/OX]$_{(TOTAL)}$ for Northumberland Street and Whitehaven Town Centre Site Measurements

	Northumberland Street				Whitehaven			
	[B/T]	[B/EB]	[B/ΣPMX]	[B/OX]	[B/T]	[B/EB]	[B/ΣPMX]	[B/OX]
	All data							
Skewness	2.6	0.1	0.9	0.9	3.3	0.0	1.0	1.5
Kurtosis	6.8	-1.2	-0.4	-0.2	11.7	-0.5	0.6	2.7
W test [1]	0.928	0.979	0.985	0.977	0.428	0.621	0.619	0.470
Mean Ratio	0.41	1.45	0.62	1.38	0.5	1.6	1.7	3.8
±1σ	0.13	0.52	0.20	0.46	0.34	0.82	1.01	2.19
	Daytime (0630-2200)				Daytime (0630-2200)			
Skewness	3.3	0.0	1.0	1.5	3.1	0.1	1.1	1.9
Kurtosis	11.7	-0.5	0.6	2.7	10.5	-0.5	1.3	3.7
	Night time (2230-0600)				Night time (2230-0600)			
Skewness	1.7	0.5	1.2	0.4	1.3	0.6	1.4	1.4
Kurtosis	2.3	-0.2	0.2	-1.0	1.0	-0.2	1.7	2.2

[1] Shapiro - Wilks W Test for normality

Frequency distributions for all data indicate good agreement in the 'shape' of the frequency distributions at each of the sites. The concentration ratio of B/Tol demonstrates a very narrow distribution compared to other ratios presented. A clear difference is also apparent between daytime and night time distribution shape parameters for B/Tol, suggesting that the small degree of scatter around the central tendency is a feature of the source term of benzene and toluene, which, in general, is significant during daytime hours only.

The Shapiro-Wilks W values indicate a large departure for ratios of BTEX at the Whitehaven site, and near normally distributed data at the Northumberland Street site. This may, in part, be attributed to the greater number of measurement collected at the latter site.

These distributions are presented graphically below. Charts 5.2 and 5.3 present the frequency distribution of [B/Tol], [B/EB], [B/ΣPMX] and [B/OX] for all measurements collected at both study sites. For visual clarity, a 2-period moving average of the

category frequency's has been added to each plot (represented as bold lines, with the data plotted as overlaying data points).

Chart 5.2 **Frequency Distributions of $[B/Tol]_{(TOTAL)}$, $[B/EB]_{(TOTAL)}$, $[B/\Sigma PMX]_{(TOTAL)}$, $[B/OX]_{(TOTAL)}$, Northumberland Street**

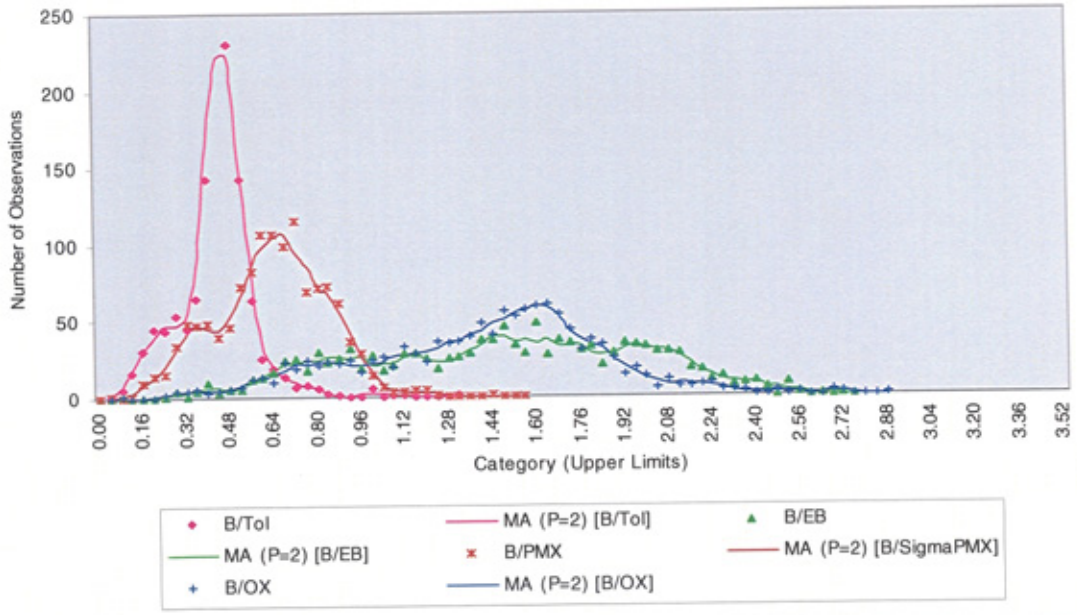
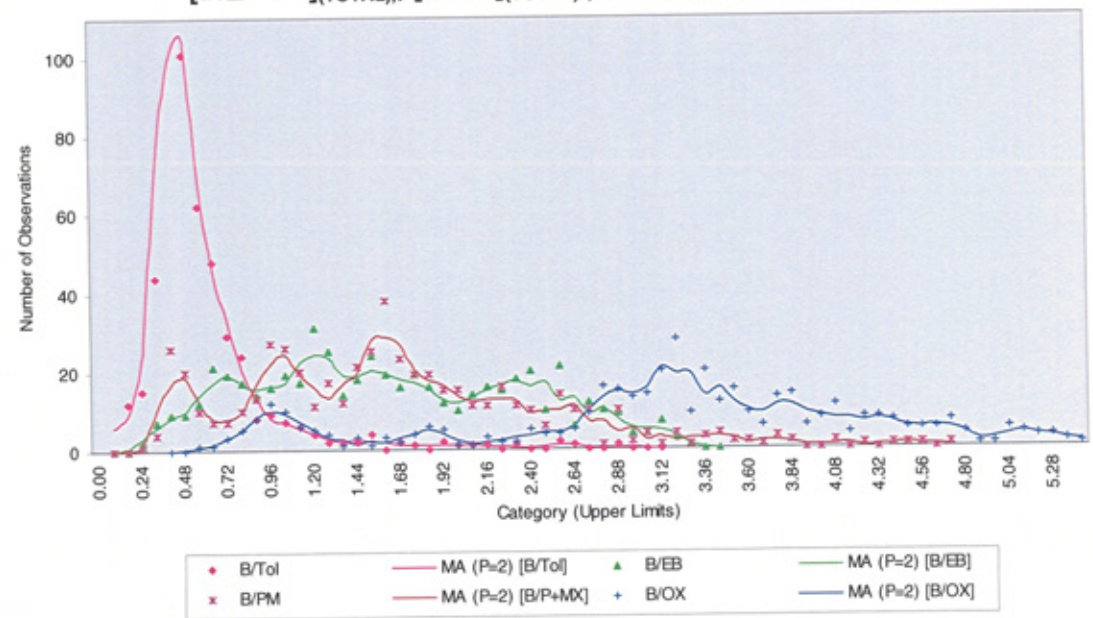


Chart 5.3 **Frequency Distributions of $[B/Tol]_{(TOTAL)}$, $[B/EB]_{(TOTAL)}$, $[B/\Sigma PMX]_{(TOTAL)}$, $[B/OX]_{(TOTAL)}$, Whitehaven Town Centre**



The above charts illustrate the relatively small degree of random scatter of B/Tol around its central tendency, than compared to concentration ratios of other aromatic hydrocarbons.

5.3.4 Time Series Analysis

5.3.4.1 Diurnal Features

Mean values of the aggregated concentration ratios of benzene with other BTEX aromatics have been calculated for each period category (using all data regardless of origin vector i.e. the 'net' diurnal profile for each study). Diurnal profiles are presented for each ratio in Charts 5.4-5.7 for Northumberland Street, and 5.8-5.11 for Whitehaven. For visual clarity, a 3-period moving average has been added, with mean values of each period plotted as overlaying points. For comparative purposes, the corresponding Σ[BTEX] value for each period category is also presented on each plot, as a 3-period moving average.

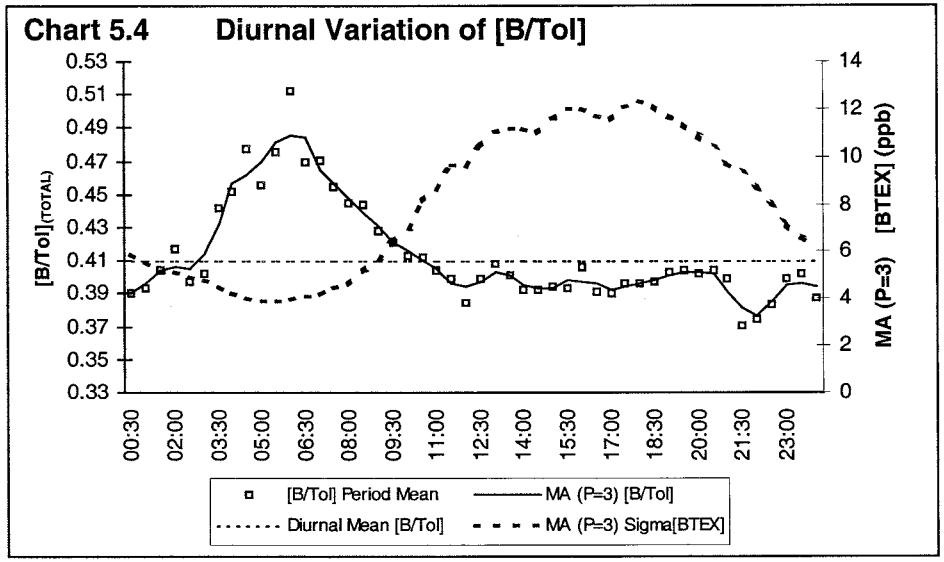


Chart 5.4 Diurnal Variation of [B/Tol]
[B/Tol](TOTAL)
MA (P=3) [BTEX] (ppb)
0.53
0.51
0.49
0.47
0.45
0.43
0.41
0.39
0.37
0.35
0.33
14
12
10
8
6
4
2
0
00:30
02:00
03:30
05:00
06:30
08:00
09:30
11:00
12:30
14:00
15:30
17:00
18:30
20:00
21:30
23:00
[B/Tol] Period Mean
MA (P=3) [B/Tol]
Diurnal Mean [B/Tol]
MA (P=3) Sigma[BTEX]

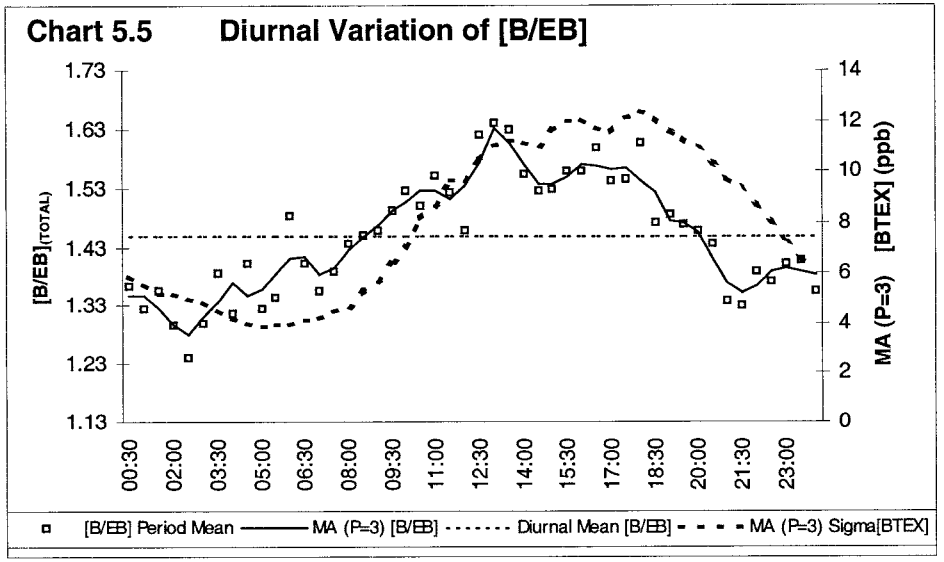


Chart 5.5 Diurnal Variation of [B/EB]
[B/EB](TOTAL)
MA (P=3) [BTEX] (ppb)
1.73
1.63
1.53
1.43
1.33
1.23
1.13
14
12
10
8
6
4
2
0
00:30
02:00
03:30
05:00
06:30
08:00
09:30
11:00
12:30
14:00
15:30
17:00
18:30
20:00
21:30
23:00
[B/EB] Period Mean
MA (P=3) [B/EB]
Diurnal Mean [B/EB]
MA (P=3) Sigma[BTEX]

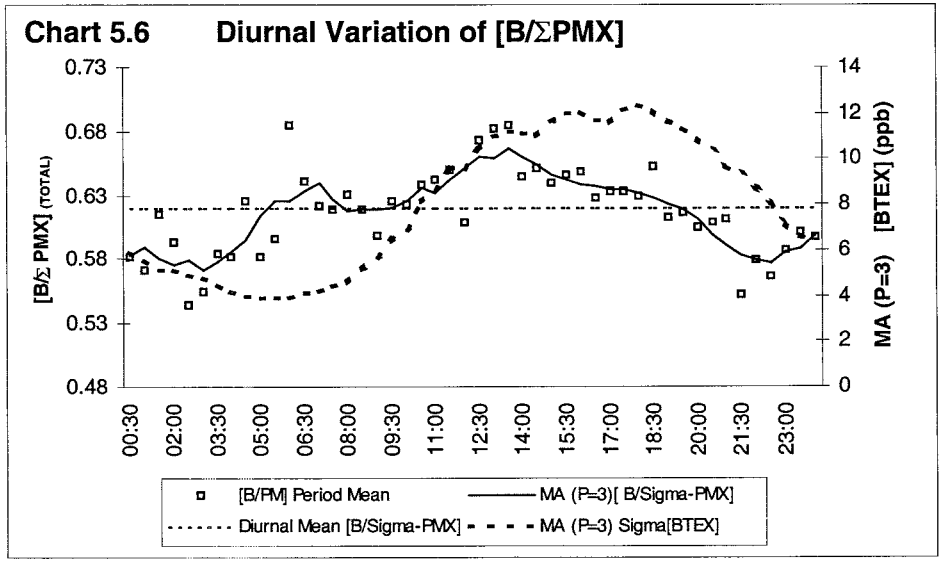


Chart 5.6 Diurnal Variation of [B/ΣPMX]
[B/Σ PMX] (TOTAL)
MA (P=3) [BTEX] (ppb)
0.73
0.68
0.63
0.58
0.53
0.48
14
12
10
8
6
4
2
0
00:30
02:00
03:30
05:00
06:30
08:00
09:30
11:00
12:30
14:00
15:30
17:00
18:30
20:00
21:30
23:00
[B/PM] Period Mean
MA (P=3)[B/Sigma-PMX]
Diurnal Mean [B/Sigma-PMX]
MA (P=3) Sigma[BTEX]

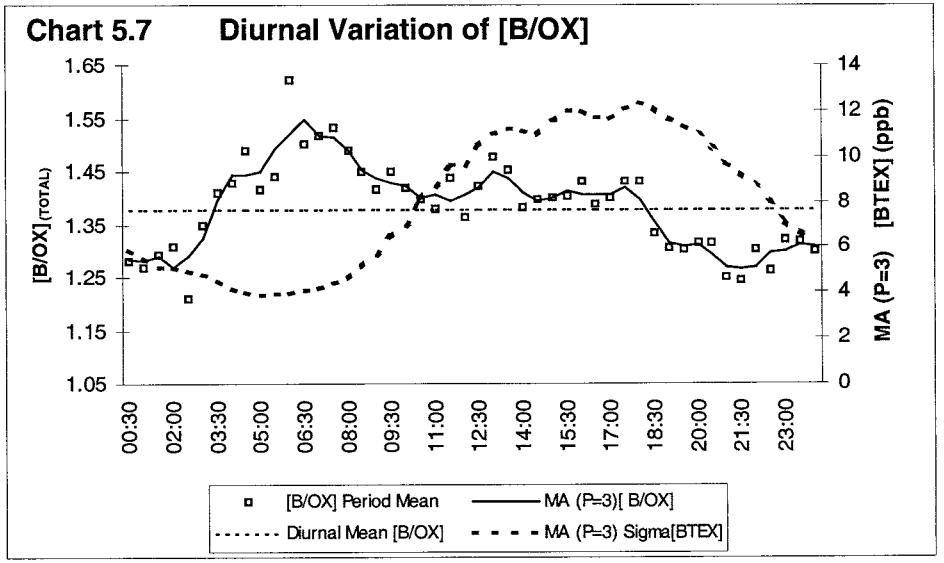


Chart 5.7 Diurnal Variation of [B/OX]
[B/OX](TOTAL)
MA (P=3) [BTEX] (ppb)
1.65
1.55
1.45
1.35
1.25
1.15
1.05
14
12
10
8
6
4
2
0
00:30
02:00
03:30
05:00
06:30
08:00
09:30
11:00
12:30
14:00
15:30
17:00
18:30
20:00
21:30
23:00
[B/OX] Period Mean
MA (P=3)[B/OX]
Diurnal Mean [B/OX]
MA (P=3) Sigma[BTEX]

Chart 5.8 Diurnal Variation of [B/Tol]

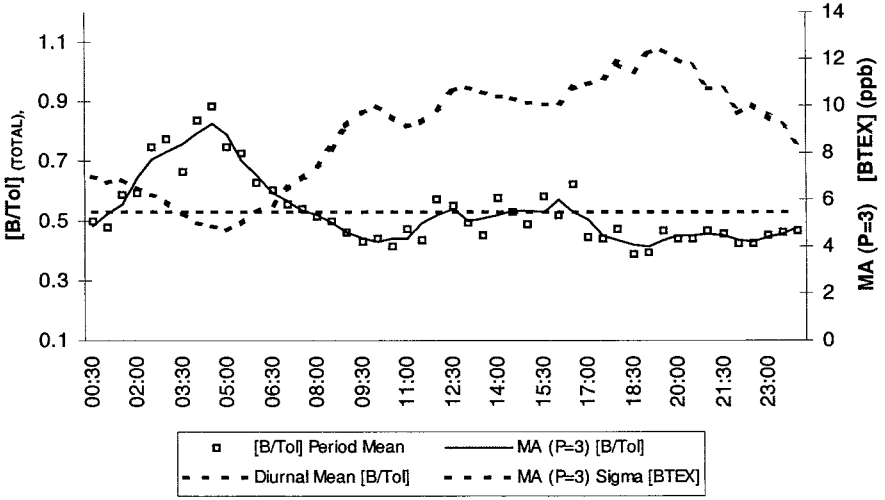


Chart 5.9 Diurnal Variation of [B/EB]

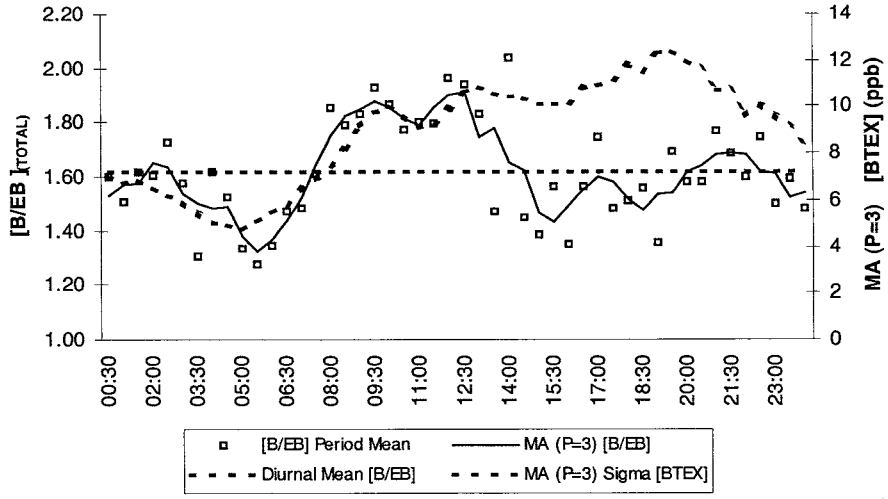


Chart 5.10 Diurnal Variation of [B/ΣPMX]

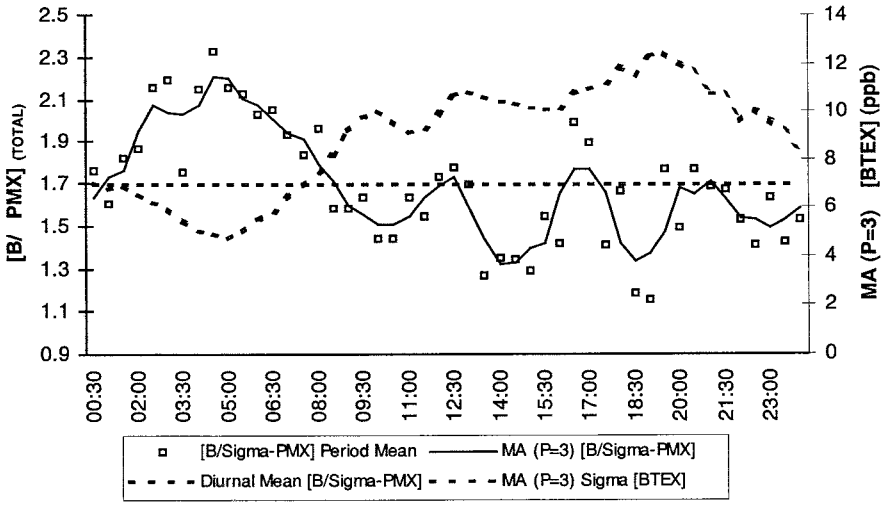


Chart 5.11 Diurnal Variation of [B/OX]

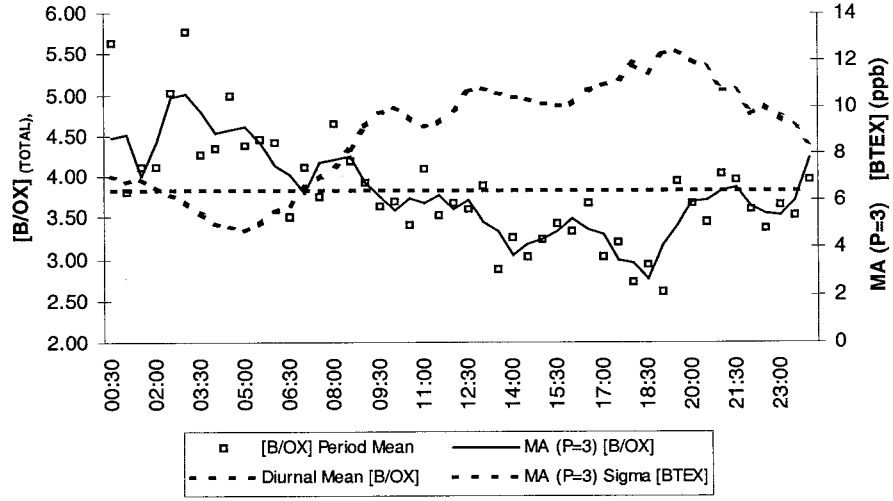


Table 5.7 presents the statistical features of mean data presented in Charts 5.4-5.11, expressed as the mean relative standard deviation ($\bar{x}\sigma'$) of each period standard deviation (σ_{0000}, σ_{0030},....σ_{2330}) of concentration ratio values, i.e. (using [B/Tol as an example):

$$\bar{x}\sigma'(\%) = 100\left(\frac{\bar{x}[B/Tol]_{(TOTAL)}}{\bar{x}_{(1\sigma_{0000},1\sigma_{0030},.....1\sigma_{2330})}}\right)$$

In addition, the mean number of measurements (n') used for each period of the time series is also included. The number of ratio values (n) averaged for each period mean ratio has been inspected to ensure that no methodological bias has occurred towards particular periods of the daily cycle, and that n values are essentially randomly distributed about the mean n value, across the 48 periods.

Table 5.7 Statistical Variance of Mean Ratio Period Values

	[B/T]	[B/EB]	[B/ΣPMX]	[B/OX]	Σ[BTEX]
Northumberland Street					
$\bar{x}\sigma'(\%)$	31.2	35.8	32.9	32.6	107.5
n'	26.3	26.3	26.3	26.3	26.3
1σ n'	1.6	1.6	1.6	1.6	1.6
Whitehaven Town Centre					
$\bar{x}\sigma'(\%)$	56.8	49.5	55.9	52.0	96.5
n'	13.3	13.3	13.3	10.7	13.3
1σ n'	0.6	0.6	0.6	0.6	0.6

1σ n' indicates the scatter of n measurements used for each period mean, over a 48 period cycle. Visual inspection indicates the distribution to be random

Values presented in Table 5.4 demonstrate a high degree of random variation (or noise), particularly for Σ[BTEX], which is to be expected, as this is the only absolute value included in this table and therefore subject to substantial variance through dispersion processes and source strength variability. Again, Whitehaven

demonstrates larger random variance for each ratio, which in part is attributable to the smaller number of measurements applied to derive each aggregated ratio.

Charts 5.4-5.7 demonstrate seasonality in the net time series at both study sites, particularly for [B/Tol], the most visually profound feature in the presented time series. A number of other ratios demonstrate a similar, nocturnal systematic deviation from mean ratio values.

A net systematic departure from the central tendency of [B/Tol] is shown to occur between 0000 and 0500, which then appears to reverse and approach the central tendency between the hours of 0500-0930. This nocturnal feature has been found to occur most prominently on a relatively small number of days, and on certain days, not at all.

Isolation of those days with greatest *systematic* deviation from the mean ratio value has been performed for [B/Tol] values for each site, using the occurrence of the peak between the hours of 0000 and 0600 as an indicator of differential behaviour of benzene and toluene. Discrimination between days showing high positive deviation from the mean ratio value (D^+), and days showing no systematic deviation from the mean (D^0) (or on a few occasions, negative systematic deviation from the mean, D^-) has been achieved by ranking each measurement day with an 'index' derived by:

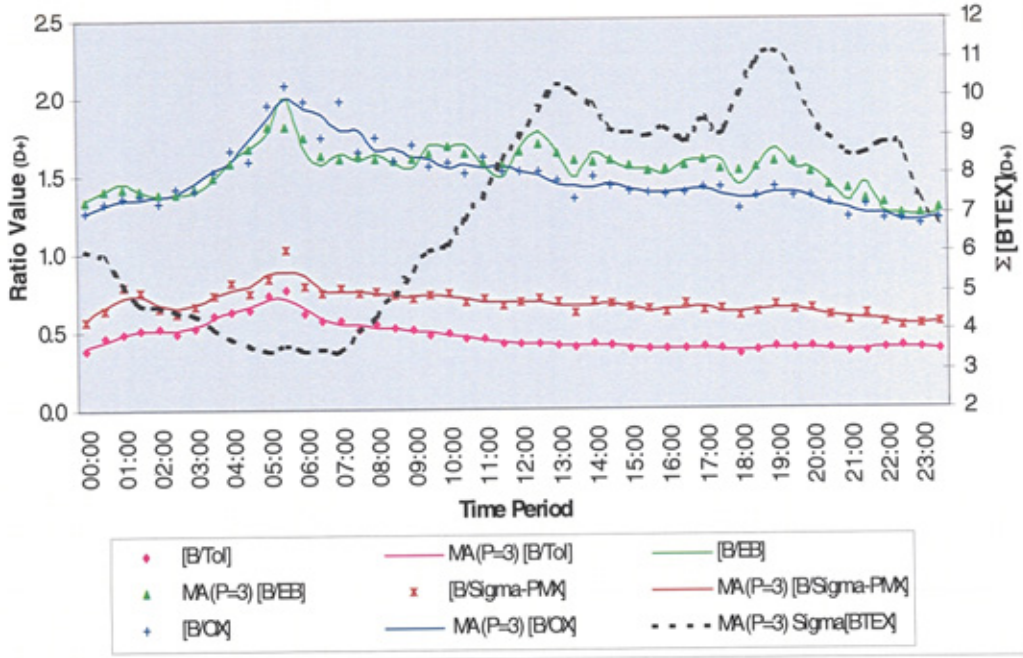
$$\text{Index} = ([\text{B/Tol}]_{(0530)}+[\text{B/Tol}]_{(0600)}) - ([\text{B/Tol}]_{(0000)}+[\text{B/Tol}]_{(0030)})$$

The use of local averaging (i.e. a mean of (0530+0600) and (0000+0030)) significantly reduces the chance of calculating index values based upon random variance in ratio values, rather than a systematic deviation.

Table 5.8 Index of [B/Tol] for Each Study Day		
Index Category [1]	Northumberland St	Whitehaven
>0.8		15.03.96
0.7 – 0.8		18.03.96, 23.03.96
0.6 – 0.7	23.12.97	16.03.96
0.5 – 0.6		17.03.96
0.4 – 0.5	27.11.97	
0.3 – 0.4	17.12.97, 30.11.97, 20.12.97	11.03.96, 09.03.96
0.2 – 0-3	26.12.97, 23.11.97	
0.1 – 0.2	28.11.97, 18.12.97, 28.12.97	12.03.96
0.0 – 0.1	21.12.97, 03.12.97, 29.12.97, 01.12.97, 02.12.97, 30.12.97, 25.11.97, 27.12.97, 22.12.97	14.03.96
-0.1 - 0.0	22.11.97, 24.11.97, 16.12.97, 25.11.97	07.03.96, 06.03.96, 10.03.96
-0.2 - -0.1	24.12.97, 19.12.97	08.03.96
[1] Index = ([B/Tol](0530)+[B/Tol](0600)) – ([B/Tol](0000)+[B/Tol](0030))		

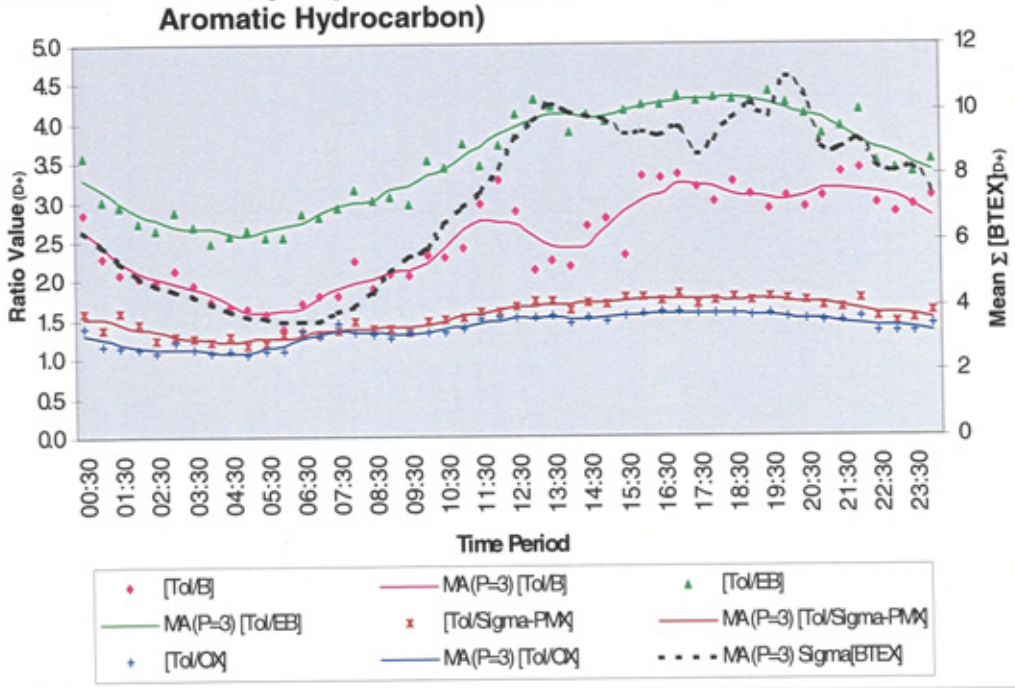
Days with index values in the upper quartile (D^+) are coloured blue in the above Table. The table suggests that the BTEX may demonstrate a wide range of systematic deviation from the central tendency. [BTEX] ratio values for these days are presented in Charts 5.12 for Northumberland Street site.

Chart 5.12 Time Series Plot of [BTEX] Ratios, D^+ Study Days, Northumberland Street



To demonstrate that the above seasonality occurring for each ratio profile is not singularly a result of the variation of the absolute concentration of benzene, ratios of the concentration of toluene with the other BTEX aromatics is presented below in Chart 5.13 for D^+ study days, Northumberland Street.

Chart 5.13 D^+ Study Days, Northumberland Street (Toluene as 'Reference' Aromatic Hydrocarbon)



5.3.5 Effect of Precipitation

Rainfall can essentially be regarded as a random event, and does not demonstrate diurnal seasonality. Therefore alternative data analysis has been applied for exploration of measurements during periods with precipitation for the Northumberland Street site.

As discussed in Section 2.3, precipitation is not believed to be a major sink for BTEX aromatics, however, calculations using Henry's Law constant indicate that precipitation scavenging may become significant during storm events of several hours, particularly in cold conditions.

Precipitation scavenging has been explored by comparison of the BTEX concentration ratios during storm events, and corresponding ratios calculated for comparable times of day from the 'net' time series. Ratios of B/Tol have been used because:

- B/Tol values demonstrate the least random variance of all ratios calculated, therefore departure from the 'net' ratio value is more likely to be statistically significant, and not through random variation; and
- although Table 2.3 demonstrates similar Henry's Law constants (K_H) for each BTEX aromatic, measurements at Northumberland Street indicate toluene is present at a mean pressure of 2.2 times that of benzene.

Days in which storm events were found to occur are presented in Table 5.9 below.

Table 5.9 Summary of Precipitation Events

Date	Mean AT [1]	Start	Stop	Precipitation (mm)	Mean B/Tol for Storm event	Net [B/Tol] [2]	PM_{10} / Σ[BTEX]	Net PM_{10} / Σ[BTEX] [3]
29.11.97	8.9	1700	0200	10.6	0.45	0.40	7.5	2.63
28.12.97	5.2	0900	1200	5.8	0.42	0.41	0.6	3.27
18.12.97	5.3	1500	2200	12.2	0.28	0.39	0.7	1.99
30.12.97	6.2	1600	2300	7.8	0.49	0.39	NA	2.05
19.12.97 to 20.12.97	7.4	0900	0500	18.8	0.41	0.40	0.7	2.74
24.12.97	7.5	1300	1700	5.6	0.42	0.40	0.5	2.28
03.12.97	2.0	1400	1600	2.0	0.49	0.40	0.8	2.35

[1] Mean air temperature on day of storm event

[2] 'Net' B/Tol for period range of storm event (see Chart 5.7)

[3] Derived from data presented in Chart 5.1

Rainfall data for Newcastle city centre provided by the Met Office

Values presented above indicate, with the exception of the storm event on the 29.11.97, that PM_{10} is removed far more efficiently than BTEX by precipitation, a feature which is widely accepted within available literature.

5.4 DISCUSSION

5.4.1 Descriptive Statistics

Chart 5.1 demonstrates a high degree of correlation between Σ[BTEX], PM_{10} and hourly averaged traffic flows along Northumberland Street. Correlation coefficients between the variables are as follows:

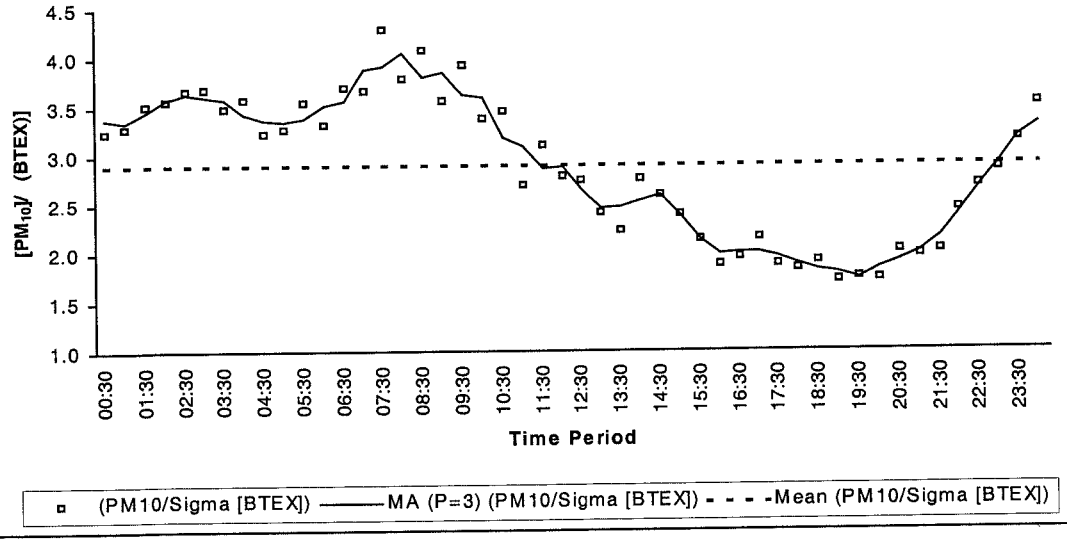
- BTEX Vs PM_{10}, r = +0.856
- BTEX Vs hourly averaged traffic flow count, r = +0.890
- PM_{10} Vs hourly averaged traffic flow count, r = +0.912

It is interesting to note that mean maximum daily concentration of BTEX is reached several hours before the maximum concentration of PM_{10}. This may be a feature of the compositional variability in traffic flow, suggesting a greater proportion of traffic is diesel fuelled at approximately 0500-0530 hours. This proposition can be visually explored (Chart 5.14), which presents the aggregated ratio of PM_{10} with Σ[BTEX]. A three period moving average has been included in the plot for visual clarity. Assuming:

- petrol fuelled vehicles emit BTEX aromatics and an insignificant mass of PM_{10}; and
- diesel fuelled vehicles emit PM_{10}, and an insignificant fraction of the total urban BTEX concentration, and that diesel fuelled vehicles are by far the predominant source of PM_{10} in urban areas [Quality of Urban Air Review Group, 1996],

then Chart 5.14 indicates that a higher proportion of diesel vehicles operate between 1930-0830 hours (positive slope) and a higher proportion of petrol vehicles operate during the day (negative slope) within Newcastle city centre.

Chart 5.14 Net $[PM_{10}]/\Sigma[BTEX]$ Profile Over the Daily Cycle



Therefore it can be concluded that the 'lag' between the two net diurnal profiles occurs due to traffic compositional variability over the daily cycle (in terms of diesel and petrol fuelled vehicles) at the Northumberland Street site. This feature may in part account for the lack of temporal correlation calculated between individual [BTEX] and $[PM_{10}]$ (Table 5.3), at the Northumberland site, even though both are predominately generated by a common source group (i.e. road traffic).

5.4.2 Aromatic Hydrocarbon Concentration Ratios

5.4.2.1 Frequency Distribution

Table 5.6 indicates that the mean ratio of individual aromatic hydrocarbon concentration in Northumberland Street illustrates reasonable agreement with those calculated from measurements collected in Sunderland City Centre. The skewness and kurtosis values demonstrate that:

- benzene shows a relatively low degree of scatter, and consequently the 'narrowest' distribution;
- other ratios demonstrate considerably broader peaks, however, with the exception of B/Tol, all show slight skew to the right of the central tendency, suggesting that they are not entirely independent variables when considered as a diurnal data set;
- the distribution of B/EB shows approximately normal distribution (in terms of the 'shape parameters') during night time and day time periods, indicating very little diurnal differentiation in the absolute concentrations of benzene and ethylbenzene. This point is interesting, as these hydrocarbons are believed to demonstrate considerably differing physical and chemical tropospheric behaviour;
- there are significant differences in the daytime and night time distributions at both measurement sites for B/Tol values, with night time values showing a greater degree of scatter from its central tendency; and
- the broadness of the distributions corroborates the residual variance calculated for aromatic ratios at kerbside sites in the previous chapter.

It is important to recognise that the degree of scatter in the distributions includes random and non-random components of BTEX aromatic concentration ratios.

5.4.2.2 Transport Vectors

The wind vector responsible for conveyance of a sample atmosphere to the collection point, is undoubtedly significant where consideration is given to absolute concentrations of a gaseous and fine aerosol species. However the use of concentration ratios may indicate processes to which a parcel of air reaching the measurement site may have been subjected to (in terms of the BTEX aromatics).

The data suggests that vector C (Table 5.5) conveyed a sample atmosphere to the ML, which had undergone partial photochemical degradation, noted by the greater ratio values calculated for each individual BTEX aromatic using benzene as the reference compound (reaction rate of benzene with ·OH is the slowest of all BTEX aromatics – Table 4.7).

At the time of this study, traffic density was very high in most southern and central parts of the city centre, whereas areas to the north of the study site consisted of open fields and suburban areas. Therefore it is likely that photochemical activity would be greater within the city centre because:

- a higher concentration of ozone would lead to higher concentrations of ·OH in the sunlit boundary layer;
- the thermal properties of an urban environment result in warmer temperatures than the surrounding suburban and rural areas, leading to higher rates of reaction of BTEX aromatics with ·OH; and
- the turbulent atmosphere of an urban environment would efficiently mix photochemical reactants;

5.4.3 Diurnal Features – Time Series Analysis

The inclusion of a moving average and the consequent removal of noise within the time series of ratios calculated for each of the study sites, permits clear demonstration of net diurnal seasonality in all BTEX ratios. (Charts 5.4-5.11). Differentiation of the relative concentrations of benzene and other aromatics should only occur as a result of physical and chemical boundary layer processes, because:

- individual BTEX aromatic emission strengths will demonstrate a degree of variability, however it is believed that such variability does not occur with seasonality in a city centre with high traffic density; and
- processes of dispersion and bulk transport are identical for each aromatic hydrocarbon.

The first statement above is particularly important, and is based upon:

- the relative proportions of BTEX aromatics from petrol vehicle emissions being approximately constant, and any deviation from a mean aromatic proportion is essentially random; and
- the fact that diesel vehicles constitute an insignificant source of BTEX (and hence the diurnal systematic variation of diesel to petrol fuelled vehicles over a daily cycle is not important in terms of individual [BTEX] ratio seasonality).

Further support to the latter supposition comes from the Whitehaven site findings, which show a similar [B/Tol] time series profile, however the locality is undoubtedly subject to considerably different traffic compositional variability over a daily cycle than the Northumberland Street site (in terms of the relative proportion of petrol and diesel vehicles).

Good agreement exists between the two sites in the general features of the net diurnal profile (or 'shape') for [B/Tol], and reasonable agreement for [B/OX], however for [B/EB] and [B/ΣPMX] there appears to be little overall similarity.

As diurnal differentiation of [BTEX] has been shown at both sites, the underlying processes which bring about differentiation, are not related to specific features of either locality under investigation. This evidence, therefore, does suggest these time series profiles occur due to the dissimilar boundary layer chemistry, or physical properties, of individual BTEX aromatics.

5.4.3.1 Indexed Study Days, Northumberland Street Site

It is surprising that the profiles of the D^+ time series may be broken down into a number of components which demonstrate reasonable linearity. Table 5.10 presents regression analysis of linear components (by least squares linear regression) of each diurnal time series cycle for [BTEX] ratios at both study sites.

Table 5.10 Linear Components of [BTEX] Ratio Time Series for D^+ Study Days

Feature Details	$[B/Tol]_{(TOTAL)}$	$[B/EB]_{(TOTAL)}$	$[B/\Sigma PMX]_{(TOTAL)}$	$[B/OX]_{(TOTAL)}$
	Northumberland Street			
Start – End	2330-0530	0200-0530	2300-0200	2300-0530
Slope	+0.030x	+0.087x	+0.053x	+0.058x
Linearity [1]	+0.964	+0.952	+0.925	+0.905
Start – End	0600-1600		0230-0530	0530-2300
Slope	-0.011x		+0.057x	-0.018x
Linearity [1]	+0.959		+0.907	+0.907
Start – End			0600-2300	
Slope			-0.006x	
Linearity [1]			+0.931	
Max. Relative Systematic Ratio Deviation (%)	+66	+30	+52	+40
	Whitehaven Town Centre			
Start – End	2300-0600	0030-0330	0000-0030	2300-0300
Slope	+0.070x	+0.069x	+0.171x	+0.429x
Linearity [1]	+0.911	+0.867	+0.927	+0.891
Start – End	0600-1230	0400-0500	0730-1900	0800-1230
Slope	-0.054x	+0.131x	-0.073x	-0.393x
Linearity [1]	+0.954	+0.902	+0.895	+0.945
Max. Relative Systematic Ratio Deviation (%)	+124	+58	+77	+95

NB Negative slope values are coloured blue

[1] Correlation Coefficient, r

The magnitude of deviation noted on D^+ study days follows the ranked order:

- B/Tol> B/ΣPMX>B/OX>B/EB at Northumberland Street; and
- B/Tol>B/OX>BΣPMX>B/EB at Whitehaven town centre site.

To explore the likelihood of these variations being attributed to the tropospheric reactivity of BTEX, Table 5.11 presents *relative* rates of reaction with ·OH and NO_3· radical species.

Table 5.11 Relative Reaction Rates of BTEX aromatics with ·OH and NO_3·

	Northumberland Street			
	1/(B/Tol) [1]	1/(B/EB) [1]	1/(B/ΣPMX) [1]	1/(B/OX) [1]
Relative reaction rate with NO_3· [2]	2.5	5.4	7.0	4.0
Relative reaction rate with ·OH	11.9 [3]	3.5 [3,4]	25.4 [3,5]	7.8 [3]
	Whitehaven Town Centre			
	1/(B/Tol) [1]	1/(B/EB) [1]	1/(B/ΣPMX) [1]	1/(B/OX) [1]
Relative reaction rate with NO_3·	2.3	6.3	2.6	2.2
Relative reaction rate with ·OH	11.1 [3]	4.1 [3,4]	9.6 [3,5]	4.4 [3]

[1] Reaction rates based upon the mean concentration of each aromatic (Table 5.2)

[2] Rate constants from Atkinson et al., 1984; Atkinson et al., 1989

[3] Rate constants from Devolder, 1994

[4] Rate constant from Simpson, 1995

[5] Rate constant from Prinn et al., 1994

The above table suggests that NO_3· is unlikely to be responsible for differentiation in the concentrations of the BTEX aromatics. However, a reasonable agreement exists between the ranked order of rates of reaction of BTEX with ·OH, and the extent of systematic deviation from the mean aromatic ratio value of the diurnal time series, particularly for B/Tol and B/EB.

However, the most significant tropospheric source of the ·OH radical is the photolysis of ozone (and to a lesser extent formaldehyde and other carbonyls) during sunlit periods of the day. However, it has been suggested that ·OH radical formation from the reaction of alkenes with ozone may be an important source (during both daytime and night time) [Paulson and Orlando, 1996], although details of a steady state concentration are not available.

5.4.3.2 Diurnal Profile of [BTEX] Ratios with Toluene as Reference Compound

The diurnal profiles of aggregated [BTEX] ratio values, calculated using toluene as the reference compound, indicate a systematic, cyclic deviation from the mean value with ethylbenzene. This demonstrates that seasonality of the net diurnal concentration ratios calculated using benzene as the reference compound does not occur through variation in the absolute concentration of benzene alone.

5.4.3.3 Consideration of Causal Processes

Meteorological and other features of indexed days are presented for the Northumberland Street site below in Table 5.12.

Table 5.12 Features of Indexed Study Days, Northumberland Street

Feature	Study Period			
	D^-	D^0	D^+	Study Mean
Calendar Influence (D-1): Weekdays	6	7	4	NA
Saturdays	0	2	2	
Sundays	1	4	1	
National Holidays	0	0	0	
Mean Σ[BTEX]$_{(0000\text{-}0630)}$ (ppb) [1]	5.2	4.7	4.4	4.7
Daily Mean Solar Irradiance (D-1) (watt m^{-2})	6.5	11.7	5.9	8.8
Mean Air Temperature $_{(0000\text{-}0600)}$ ($^{\circ}$C) [1]	7.4	5.2	6.8	6.2
Mean [PM_{10}]$_{(0000\text{-}0600)}$ (μgm^{-3}) [1]	15.1	16.6	18.9	16.8
Primary / Secondary Wind Vector (Table 5.4)	A/B	C/A	C/A	NA

'D-1' indicates solar flux of the previous calendar day

[1] Differences between means are not statistically significant at the 95% confidence interval level

The information above appears to suggest that wind vector is important, which infers the origin and 'history' of a sample may be important. However other meteorological features appear not be significant within this data set.

5.4.4 Precipitation Scavenging

It was noted within experimental data that the relative removal rate of PM_{10} is much greater than for BTEX aromatics. B/Tol values presented in Table 5.9 do suggest that toluene is removed at a slightly faster rate than benzene during storm events, which agrees with theoretical calculations based upon their corresponding relative pressures during such storm events and experimentally determined Henry's Law constants (Section 2.3).

However, the degree of differentiation is very small, and is not apparent within absolute concentrations during these storm events. These findings confirm that BTEX aromatics are not significantly scavenged by precipitation, even during cold days and intense rain.

5.5 CONCLUSIONS

This chapter has demonstrated that aggregated ratios of aromatic hydrocarbons provide a means of exploring the relative behaviour of BTEX over a daily cycle, features which are not apparent within time series of absolute concentrations of these compounds.

The 'shape' parameterisation of frequency distributions of concentration ratio values indicated the degree to which changes in ratio values are random and non-random, and have corroborated the estimates of residual variance in the source emission term, calculated for kerbside sites presented Chapter 4. The 'shape' parameters have suggested that benzene and toluene show relatively small variation in the source composition term in traffic polluted atmospheres.

Although frequency distributions show a degree of normality for ratios calculated from measurements collected at the Northumberland Street site, all distributions ratios indicate a slight skew to the right, from which it can be concluded that these variables are not entirely independent. This feature has been corroborated by time series analysis of such ratio values, which has shown that through aggregation of many days of data, and with considerable reduction of noise, diurnal systematic departure from a ratio 'mean' value becomes apparent.

Although no single cause can be determined which satisfactorily accounts for these departures, it can be concluded with a good degree of certainty that traffic compositional variability (and therefore source compositional variability) was not responsible. This statement (that source variability does not cause differentiation of relative BTEX concentration) is supported by additional experimental evidence in Chapter 7. Another source emission strength related factor, the distribution of calendar events over indexed dates, has also been rejected as a possible cause of differentiation.

It is concluded that one or a combination of the following processes may have been responsible:

1. Night time ·OH radical generation and corresponding reaction with BTEX aromatics. Literature confirming the phenomenon of reaction of BTEX aromatics with ·OH in darkness is not known;
2. Transport of BTEX from other areas bearing a differing proportion of each aromatic (perhaps by extensive photochemical ageing away from the measurement sites). This proposition is supported by the fact that wind vector reaching the Northumberland Street site during D+ days appears to be important; and
3. Absorption within a liquid organic layer, which may exist upon carbonaceous aerosol. Although no convincing evidence emerges from the studies presented within Chapter 5 to support this suggestion (other than nocturnal [BTEX] differentiation tended to occur on mornings with high [PM_{10}]), and that this process is somewhat hypothetical, it cannot be excluded by the experimental data.

Points 1 and 2 are explored further in Chapter 7, where collection of [BTEX] was performed within an isolated environment, so that the second process can effectively be ignored. The third proposition is considered in the following chapter, through characterisation of diesel exhaust carbonaceous combustion aerosol.

6 CHARACTERISATION OF DIESEL CCA

6.1 INTRODUCTION

Chapter 2 introduced the concept of exchange of BTEX aromatics at the surface of Carbonaceous Combustion Aerosol (CCA), an accepted phenomenon for many SVOCs. Available literature generally describes the retention of organic molecules upon CCA as being a process of adsorption, and have ignored the occurrence of, and the significance of, an organic liquid phase associated with such aerosol. The presence of a liquid film may infer that compounds, which are normally present in the gas phase at room temperature, such as BTEX aromatics, may be associated with CCA in particular environments. This chapter describes a study of aged diesel CCA to explore:

- the ratio of OC to 'core components' (black and elemental carbon, noted as BC+EC hereafter) in settled dust samples which are rich in diesel aerosol;
- the physical state and extent of extractable OC associated with CCA;
- the composition of this organic fraction by using 'solvent free' VOC and SVOC collection and GCMS analysis; and
- the occurrence of gas-CCA distribution of BTEX.

In order that the above objectives were met, it was necessary to collect a large quantity of diesel CCA. However, collection by filtration of urban air would not satisfy the above requirements because:

- Eautough and co-workers (1995) have indicated that sampling of carbonaceous aerosol by filtration leads to a loss of 'significant concentrations' of aliphatic,

acidic and aromatic organic compounds from the filter-retained sample. Their study concluded that greatest losses occurred for compounds demonstrating the highest vapour pressures (i.e. those of particular interest in this investigation);

- samples collected by filtration of urban air would comprise a number of material types from a wide range of sources (Figure 2.3); and
- that collection of a suitable mass of aerosol for a wide range of tests (~500mg) would take many days, even sampling at very high flow rates.

For these reasons it was decided to collect and analyse deposited diesel aerosol, which had been exposed to traffic emissions for a considerable amount of time.

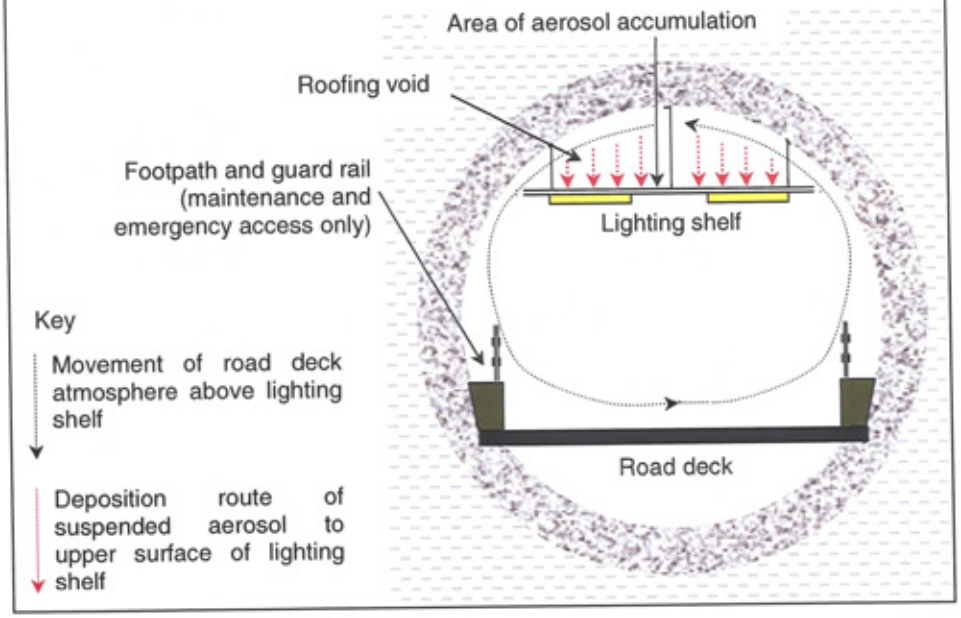
6.2 SAMPLING OF CARBONACEOUS AEROSOL

6.2.1 Deposited Aged CCA – The Tyne Tunnel Site

Deposited carbonaceous aerosol samples were collected from the lighting shelf void space within a road tunnel in Tyneside (the Tyne Tunnel). The Tyne Tunnel serves as Newcastle upon Tyne's road link between East Howden (located at the north bank of the river Tyne) and East Jarrow (located at the south bank of the River Tyne), and is approximately 1400m long. At the time of this study, the tunnel conveyed all road traffic types to flows of typically 36000 vehicles per day.

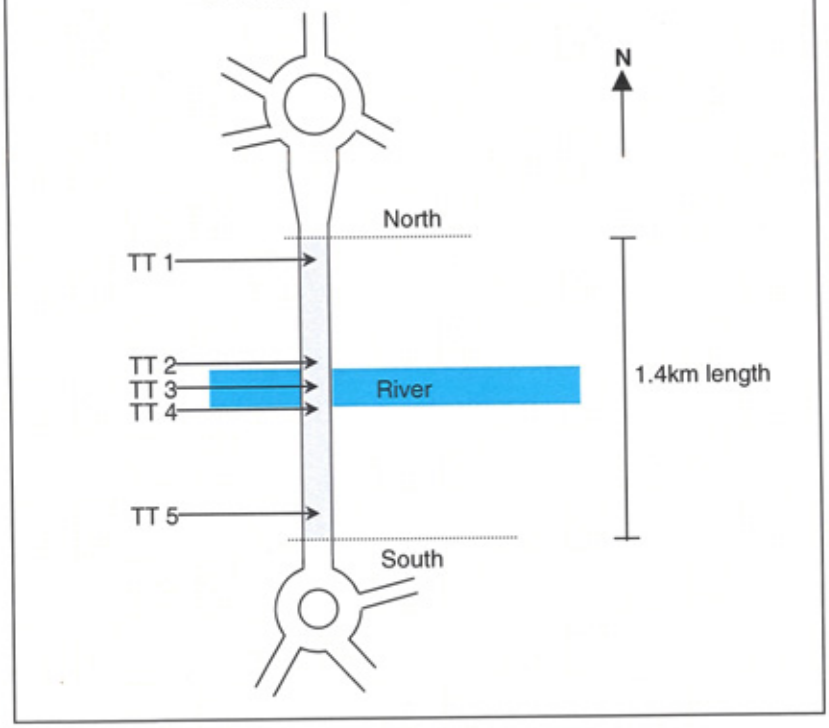
The lighting shelf (as indicated in Figure 6.1) provided a surface upon which aerosol generated by road traffic had deposited to over an estimated period of 8 years, leading to a 5-8mm deposit.

Figure 6.1 Cross Section of the Tyne Tunnel, Indicating Lighting Self Sampling Area



As the concentration of diesel aerosol in the tunnel is high, even during night time periods, it is unlikely that other sources of aerosol would be significant at the sampling points chosen within the tunnel (Figure 6.2).

Figure 6.2 Settled Dust Sampling Locations, Tyne Tunnel



Samples were collected between 2200-2330 hours, 23rd July 1997. Inspection of, and sample collection from, the lighting shelf was achieved by means of a service crane (northbound traffic was temporarily halted during the operation). Samples were collected into gas tight glass containers and refrigerated upon return to the laboratory.

Measurements at the tunnel centre (collected several weeks after the sampling exercise) indicated the sample materials were subjected to a mean air temperature of 17.4°C (n=35).

6.2.2 Other Sample Material

6.2.2.1 TEOM Filter Cartridge

For comparative purposes, a TEOM filter was also subjected to analysis (SPME-GCMS) only. The TEOM filter was used for PM_{10} collection at the Whitehaven Site (described in Chapter 5) for period of 24 days (which equates to a sample volume of 103.7±5.1m^3).

6.2.2.2 Non-Aged Diesel Aerosol

Diesel soot, removed from the exhaust of a 1995 Citroen Aura Diesel vehicle, was also collected and subject to analysis as described in Table 6.1 (SPME-GCMS only).

6.3 EXPERIMENTAL DETAILS AND RESULTS

This section presents and discusses the methodological approach and results of a wide range of analyses carried out on the sample materials detailed in Table 6.1

Table 6.1 Sample Descriptions

Sample Name	Sampling Location	Quantity Collected (g)	Description
Tyne Tunnel Samples			
TT 1	Upper surface of lighting shelf, north bank entrance	1.71	A very fine, black powder with occasional particles of mica and fine-coarse sand. The sample had a strong odour with an oil-like character.
TT 2	Upper surface of lighting shelf, tunnel centre	5.30	
Tt 3	Upper surface of lighting shelf, tunnel centre	1.25	All Tyne Tunnel dusts had a similar powdered, black appearance.
TT 4	Upper surface of lighting shelf, tunnel centre	1.62	
TT 5	Upper surface of lighting shelf, south bank entrance	1.81	
Other Samples			
TEOM 1	Suburban Background [2] Whitehaven Town Centre	0.0043	Dark grey – black with slightly grainy surface with occasional grains of sand and mica
Exhaust 1	1995 Citroen Aura Diesel exhaust pipe	1.41	Black coarse powder with very strong hydrocarbon odour

[1] Calculated using mean [PM_{10}] for the Whitehaven study, at a constant 3 l min^{-1} flow rate

[2] See Appendix 5 for locality definitions

It was anticipated that the composition of collected aerosol samples would be considerably diverse, and hence were subjected to a wide range of analytical tests, as described in Table 6.2.

Although not forming pivotal analytical methodologies used throughout this research, a brief description of each of the above techniques is provided below. These techniques have been extensively documented elsewhere, and the Reader is directed to the following example texts for further information: thermal methods [Hatakeyama and Zhenhal, 1998]; XRF Spectroscopy [Whiston, 1987]; GC-MS [Karasek and Clement, 1988]; ASE [Dean, 1998]; and SPME [Dean, 1998; Zang et al., 1994].

Table 6.2 Analytical Techniques Applied to Samples

Technique	Objectives	Samples Studied
	Sample Extraction and Analyte Collection	
Accelerated Solvent Extraction (ASE)	• To extract a maximum quantity of OC from sample aerosol, and identify main components by GCMS • To provide a semi-quantitative identification of principal OC components	TT1-TT5
Solid Phase Micro Extraction (SPME)	• Provide a 'solvent free' method of collection of VOCs and SVOCs from sample materials	Exhaust 1, TT1&5, TEOM 1
	Sample / Extract Analysis	
Thermogravimetric analysis (TGA)	• To identify the proportion of carbon in collected aerosol samples	TT1–TT5
Differential Thermal Analysis (DTA)	• To identify the proportion of volatile and non volatile components	TT2
Energy Dispersive X-ray Fluorescence (EDXRF)	• To identify metals and their compounds within a representative aerosol sample	TT2
Gas Chromatography Mass Spectrometer (GCMS)	• To characterise volatile and semivolatile OC components from SPME collection and solvent extracts.	All

6.3.1 Energy Dispersive X-ray Fluorescence Spectroscopy

XRF is a spectroscopic method that is commonly used for solids, in which secondary X-ray emission is generated by excitation of a sample with X-rays. XRF was applied to identify (qualitatively) elemental species within Tyne Tunnel samples, and to indicate which elements constituted molecular species with boiling points of less than 1000°C.

6.3.1.1 Experimental

Samples were already satisfactorily powdered and required no sample preparation. The samples were placed in the sample chamber of an XRF spectrometer (XR300 EDXRF Spectrometer), and were irradiated with primary X-rays (X-ray tube of 10-100W, with operating energy range of 30 or 50 KeV). As the amount of X-ray

fluorescence generated is very sample dependent, and quantitative analysis requires calibration with standards that are similar to the sample matrix, values are only considered of a qualitative nature only. The working range of this system was an relative atomic mass of between 28 and ~235 (i.e. from silicon to ~uranium).

EDXRF analysis was performed on sample TT2. In addition, this sample was then heated to 1000°C in a non-oxidative atmosphere (argon), and underwent additional EDXRF analysis (this heated sample is noted as TT2H hereafter).

6.3.1.2 Results

EDXRF analysis shows the presence of the following elements:

TT2 (unmodified): Fe, Ca, Pb, Br, Cl, Ti, Cr, Mn, K, Ni, Cu, S; and

TT2H (heated sample) Fe, Ca, Ti, Cr, Mn, K, Ni, Cu, S.

6.3.2 Thermal Methods

6.3.2.1 Thermogravimetric Analyses (TGA)

This method is useful for determining sample purity and water, carbonate, and organic content; and for studying decomposition reactions [Whiston, 1987]. Thermogravimetry has been applied to determine the total carbon content of each of the samples, in addition to identifying the extent of volatile matter present within the sample matrix.

Experimental

TGA was performed using a Stanton-Redcroft TG-750 Thermobalance. In each analysis a sample mass of between 5-10 mg was used, and placed within a platinum crucible. A heating rate of 20°C minute^{-1} was used for all sample materials, under

oxidative (air) and non-oxidative (argon) atmospheres, to 1000°C. Atmosphere flow rates were 10 ml minute^{-1}. Sample mass changes were logged by chart recorder.

6.3.2.2 Differential Thermal Analysis (DTA)

This method was applied to identify endothermic and exothermic processes, which include phase transitions, dehydration, decomposition or solid-state reactions.

Experimental

DTA was performed using a Stanton-Redcroft DTA 673. In each analysis a sample mass of between 5-10 mg was used, and placed within a platinum crucible. A heating rate of 20°C minute^{-1} was used for all sample materials, under an oxidative (air) atmosphere to 1000°C. Atmosphere flow rates were 200 ml minute^{-1}. Sample mass changes were logged by chart recorder.

6.3.2.3 Sample Preparation for Thermal Analysis

The Tyne Tunnel dust samples, being of a fine powdered form, required no preparation. In addition to unmodified sample dusts, 0.5g of sample TT2 was shaken for 5 minutes with 5ml acetone (HPLC grade). This process was repeated four times, and supernatants were combined and allowed to stand at room temperature in an open vessel for 24 hours, to remove acetone. The sample solid was dried at 80°C for three hours to remove residual acetone. Both the extract (a dark brown mobile oil, noted as TT2E hereafter) and the acetone-washed TT2 sample (noted as TT2AW hereafter) were analysed separately using thermal methods as described above.

Details of thermal analysis of each of these samples are presented in Table 6.3 below.

Table 6.3 Thermal Analysis Details				
Sample No.	**Analytical Technique**	**Heating Rate [1]**	**Atmosphere**	**Sample Form**
TT1	TGA	20° min^{-1}	Air	Dust (unmodified sample)
TT2	TGA	20° min^{-1}	Air	Dust (unmodified sample)
TT2AW	TGA	20° min^{-1}	Air	Acetone washed dust
TT2	TGA	20° min^{-1}	Argon	Dust (unmodified sample)
TT3	TGA	20° min^{-1}	Air	Dust (unmodified sample)
TT4	TGA	20° min^{-1}	Air	Dust (unmodified sample)
TT5	TGA	20° min^{-1}	Air	Dust (unmodified sample)
TT6	TGA	20° min^{-1}	Air	Dust (unmodified sample)
Carbon	TGA	20° min^{-1}	Air	Activated carbon standard
TT2	DTA	200° min^{-1}	Air	Dust (unmodified sample)
TT2AW	DTA	200° min^{-1}	Air	Acetone washed dust
TT2E	DTA	200° min^{-1}	Air	Acetone extract of TT2
[1] From ambient to 1000°C in each analyses				

6.3.2.4 TGA Results

Table 6.4 below presents a summary of sample mass loss due to heating to 1000°C.

Table 6.4 TGA Summary					
Sample ID. / Atmosphere	**Mass Loss (%)**				
	20-200°C	**201-400°C**	**401-700°C**	**701-1000°C**	**20-1000°C**
TT1 / Air	4.0	9.0	16.0	6.0	35.0
TT2 / Air	5.0	10.0	19.0	3.0	37.0
TT2AW / Air	5.0	7.0	11.0	4.5	27.5
TT2 / Argon	4.0	7.0	7.0	17.0	35.0
TT3 / Air	4.5	6.0	23.0	5.0	38.5
TT4 / Air	5.0	17.0	22.0	4.0	48.0
TT5 / Air	6.0	12.0	16.0	4.0	38.0
Carbon / Air	3.3	1.0	86.5	4.0	94.8

TGA data above has demonstrated a degree of compositional commonality in the Tyne Tunnel samples. The above table also suggests a significant proportion of all

tunnel dust samples is carbonaceous. As much mass loss from each sample occurred at temperatures below which oxidation of carbon begins, the data indicates a significant proportion of volatile material was also associated with each sample.

6.3.2.5 DTA Results

Table 6.5 presents the results of DTA analysis of TT2, TT2AW, and TT2E.

Table 6.5 DTA Summary

Sample No. / Atmosphere	Process Feature Number [1]			
	1	2	3	4
TT2 / Air	100-240°C, Endo, Area = 16	NA	240-290°C, Endo, Area = 24	290-690°C, Exo, Area = 3000
TT2AW / Air	120-230°C, Endo, Area = 18	230-265°C, Endo, Area = 19	265-325°C, Endo, Area = 38	325-700°C, Exo, Area = 1600
TT2E / Air	100-290°C, Endo, Area = 29	NA	NA	290-670°C, Exo, Area = 650

[1] Exo = Exotherm; Endo = Endotherm;

Endothermic processes represent phase changes, which, within a sample containing diesel CCA, may be attributed to:

- evaporation of Liquid Organic Carbon (LOC); and
- melting of Solid Organic Carbon (SOC).
- decomposition of LOC to SOC / EC / BC (non-oxidative); and

Exothermic processes can be attributed to:

- oxidation of LOC, SOC, and other carbonaceous matter to CO_2.

Between ca. 290-700°C, the large exotherm is likely to have arisen from the oxidation of carbonaceous matter forming CO_2 (typical $\Delta_f H^\ominus$ = -393.6 kJmol^{-1}) and if hydrogen containing organic matter, H_2O (typical $\Delta_f H^\ominus$ = -285.8 kJmol^{-1} [Chase, 1998])

Phase change processes occur at a much lower energy level e.g. $\Delta H^\ominus_{VAP}$ tridecane = +63KJmol^{-1} [Majer and Svoboda, 1985]. Phase changes are therefore likely to account for the relatively small endotherms between ca. 100-400°C in the sample, resulting most probably from the OC fraction, and possibly water associated with the sample material.

Analysis of the extract of sample TT2 demonstrates that extractable organic matter comprises both a volatile and non-volatile component (noted by the endotherm and exotherm respectively).

6.3.3 Chromatographic Analysis

6.3.3.1 Accelerated Solvent Extraction (ASE®)

Accelerated solvent extraction is a technique for extracting solid samples with liquid solvents. ASE was applied for efficient extraction of OC associated with the Tyne Tunnel samples, allowing the main components of the OC to be characterised by GCMS analysis.

Experimental

Tyne Tunnel dust samples were accurately weighed (approximately 0.5g) into a stainless steel extraction cell (11ml capacity). Dead volume within the cell was reduced using an inert solid (Hydromatrix). Extraction was carried out using an Automated ASE system from Dionex Corporation. Extraction with acetone (HPLC grade) was performed at 2000psi and 100°C; with a static extraction time of 5 minutes (total of three extractions), and a total extraction time 30 minutes. A final

extract volume of between 5-7ml was obtained for each sample, which was reduced at room temperature for 24 hours. The resulting extract was weighed, then dissolved in 5ml acetone, and subjected to GCMS analysis as described below. An injection volume of 1μm of sample solutions was used in each GCMS analysis.

6.3.3.2 Solid Phase Micro Extraction

SPME involves exposing a fused silica fibre, which has been coated with a non-volatile polymeric coating, to a sample headspace. The absorbed analytes are thermally desorbed in the injector of a GCMS system for separation and quantitation [Pawliszyn, 1995]. The purpose of using SPME was to collect predominately volatile and semi-volatile OC compounds from the sample matrices, and achieve 'solvent-free' delivery of collected analytes to a GCMS system. The solvent-free approach is important, as volatile analytes typically co-elute with common extracting solvents.

Experimental

Samples were accurately weighed (approximately 0.2g) into a 15ml glass vessel, which was then sealed with a septum. The sample vial was heated using a waterbath to 80°C, and the SPME fibre (30μm polydimethylsiloxane coating, preconditioned within a GCMS injection port, at 250°C under a helium flow for 10 minutes) was inserted into the headspace, and allowed 10 minutes equilibration time. The vessel was then allowed to cool to room temperature. After an additional 5 minutes, the SPME fibre was retracted, and immediately transferred to the injection port of a GCMS system (described below). Desorption temperature was 250°C.

6.3.3.3 Gas Chromatography – Mass Spectrometer Detector

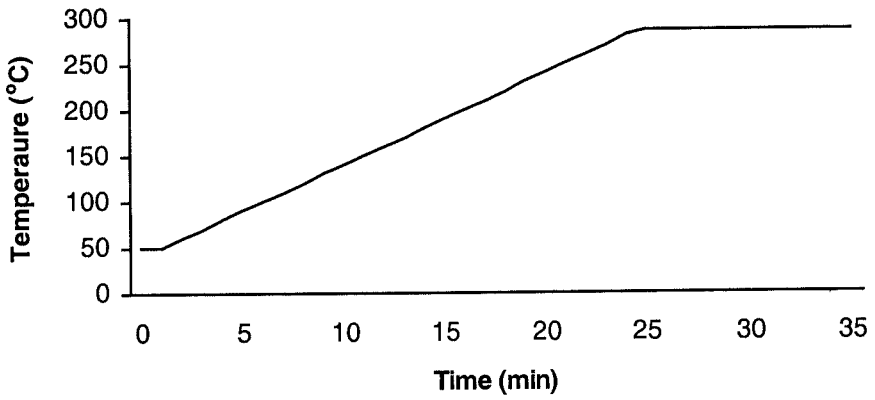
Introduction

Mass spectrometry was applied for quantitation and identification of solvent extracted OC compounds, and analytes collected by SPME headspace sampling.

Experimental

Either an injection of solvent extract or SPME fibre achieved introduction of sample analytes into the GCMS system (Hewlett Packard G1800A GCD System). Analyte delivery to the GCMS system by either route underwent separation on a 30m x 0.25mm i.d. DB1 capillary column (polysimethylsiloxane stationary phase), with He carrier gas (1ml min^{-1}, >99.999%). The oven temperature programme applied for this study is shown in Chart 6.1 below. Where an acetone solution was injected, a solvent delay of 5 minutes was applied. The ramp rate was 9°C min^{-1}.

Chart 6.1 GCMS Oven Temperature Program



6.3.3.4 GCMS Results – ASE Sample Delivery

Reduction of all acetone extracts at room temperature yielded a dark brown oil, which became mobile upon heating above 40°C. The mean proportion of extractable mass by means of ASE was found to be 13.7±3.1% (1σ).

Table 6.6 presents the principle components identified within acetone solutions of reduced sample extracts, and indicates the approximate relative abundance and boiling point of each.

6.3.3.5 GCMS Results – SPME Analyte Delivery

Table 6.7 below presents a summary of analytes identified by SPME collection and GCMS analysis, which includes the approximate relative abundance of each species collected by the SPME fibre coating. It is important to recognise that this value does not necessarily represent the concentrations of each within the sample matrix, and is a function of:

- the vapour pressure of each compound (which is related to the concentration in the sample, and the compounds volatility);
- the affinity of each compound to the sample matrix; and
- the affinity of each compounds for the stationary phase of the SPME fibre.

Table 6.6 Summary of GCMS Analysis of ASE Extracts of Tyne Tunnel Dust Samples

Name	Physical Properties of Sub Group				Relative Abundance (%) [6]					
	RMM Range [2]	T_M (°C) Range [2,3]	T_B (°C) Range [2,3,4]	PS@RT [5]	TT1	TT2	TT3	TT4	TT5	Mean
C9-C10 Alkanes [1]	128-142	-53 - -30	150 – 174	Liquid	6.2	0.0	0.0	6.2	0.0	12.4
C11-C1 Alkanes [1]	156-226	-26 – 18	196 – 287	Liquid	48.3	6.1	1.9	71.7	1.0	28.8
C16- C20 Alkanes [1]	226-282	18 – 37	287 – 343	Solid	2.3	10.5	14.5	0.9	20.2	9.7
C21-C25 Alkanes [1]	297-353	41 – 53	357 – 402	Solid	0.5	10.3	23.2	0.0	5.1	7.8
C6-C10 Cycloalkanes [1]	84-140	81 – 202	84 – 140	Liquid	0.9	1.1	0.0	3.3	0.0	1.1
PAH (nB =2-3)	128-178	81 – 218	218 – 340	Solid	3.2	5.0	6.6	1.3	0.0	3.2
PAH (nB=4-5)	202-252	156 – 255	404 – 495	Solid	0.8	0.0	1.5	0.0	0.0	0.5
Benzoic acid	122	122	249	Solid	1.5	0.0	0.0	0.0	0.0	0.3

[1] Includes alkyl derivatives
[2] Ranges of non alkylated hydrocarbons
[3] Weast and Grasselli, 1989; Majer and Svoboda, 1985
[4] At 1 atmosphere pressure
[5] Physical state at room temperature (25°C)
[6] Abundance of identified components compared to the sum of all peak areas

nB - number of benzene rings
T_M – melting point
T_B – boiling point

Table 6.7 Summary of GCMS Analysis of Sample Head Space by SPME (species ranked by vapour pressure)

Name	Physical Properties of Sub Group					Relative Abundance (%)			
	RMM ($gmol^{-1}$) [3]	T_M (°C) [4]	T_B (°C) [4, 5]	P_{VAP} (Pa, 298K)	PS@RT [10]	TT2	TT5	TEOM	Diesel Soot
Trimethyl benzene [1]	120	-45 - -25	165 – 175	225-351 [7]	Liquid		++		
2-Ethyltoluene	120	-17	164	347 [6]	Liquid		+		
Isobutyric acid	88	-46	155	241 [6]	Liquid	+			
n-Butylbutyrate	144	-92	166	241 [6]	Liquid	+++			
Acetophenone	120	19.6	201	53 [6]	Liquid			++	
C11-C16 Alkanes [2]	156-226	-26 - 18	196 – 287	0.2-50 [8]	Liquid	+++	++++	+++	+++
2-Ethylphenol	122	-18	204	20 [9]	Liquid	+			+
3-Methylphenol	122	12	202	13 [9]	Liquid				+
Dimethylphenol [1]	122	27	211	NA	Solid				++
Trimethylphenol [1]	136	92	231	NA	Solid				+
Nonanal	142	-18	191	NA	Solid	+			
C13-C16 Alkylbenzene	176 – 218			NA	Solid			+	
C17+Alkylbenzenes	232+			NA	Solid			++++++	
C17+ Alkanes [2]	226+	18+	287+	NA	Solid	++++	++++++	++++	++
a-Terpineol	154	12	219	UA	Liquid	+			
Isopropyl myristate	270		167	NA	Solid	+		++++	
Butylated hydroxytoluene	220	71	205	NA	Solid			++	
Dibenzofuran	169	81	285	NA	Solid				++
PAH [2]	128-252	81 - 255	218 - 495	NA	Solid		++		+++++++

[1] All structural isomers [2] Includes alkylated derivatives within 15% of the group maximum n-alkane RMM [3] Ranges indicate n-alkanes in category

[4] Weast and Grasselli, 1989; Majer and Svoboda, 1985 [5] At 1 Atm [6] Daubert and Danner, 1989; [7] Chao et al., 1983 [8] Biddiscope, 1963

[9] Abraham, 1994 [10] Physical state at room temperature (20°C)

TM – melting point T_B – boiling point P_{VAP} – vapour pressure

Note: NA = <10Pa; UA = unavailable; and (+ to +++++++) indicates the relative abundance of each species collected by the SPME fibre from sample headspaces

6.4 DISCUSSION

6.4.1 Elemental Composition

Sample TT2 demonstrated a range of metals to be present. Heating the sample to 1000°C reduced the concentrations of lead, chlorine and bromine to below detectable limits. This suggests that lead had been present mainly as $PbCl_2$ and $PbBr_2$, products of the combustion of leaded petrol fuels, which have boiling points of 950 and 916°C respectively [Stull, 1947; Weast and Grasselli, 1989].

6.4.2 Carbon Content of Tyne Tunnel Dust Samples

The TGA profile for powdered activated charcoal indicates that under the conditions applied for this and other TGA analysis, carbon is almost completely oxidised at temperatures below 700°C, with 85% of this mass loss occurring between 550-700°C. Oxidative loss of carbon mass appears to begin significantly at 400°C.

Upon this basis, it can be assumed that the majority of mass losses up to this point in the Tyne Tunnel samples can be attributed to the evaporation or oxidation of carbon containing matter in the sample material, in addition to:

1 loss of associated water. The water content of the samples is difficult to determine from the findings of this investigation, however it is believed to be small, as a mean mass loss of <0.5% was noted for all samples below 100°C, which represents loss of both organic and water components; and

2 loss of Pb, Cl and Br (indicated by EDXRF analysis of TT2). It has been postulated that these elements comprise molecular species, which have boiling points of less than 1000°C. However their loss is expected to occur about 900°C, therefore such loss has not contributed to mass loss profiles associated with thermal processes of carbon.

Therefore it is concluded that the mean carbon content of samples from the Tyne Tunnel is 39.5±6.8% (1σ, n=5) by mass.

EDXRF analysis of TT2 indicated the remaining highly unreactive and involatile mass is likely to be wind blown dust (crustal material and dusts generated from the road surface), components of sea spray, and other non-volatile inorganic compounds of anthropogenic and natural origin [Caens et al., 1998; Quality of Urban Air Review Group, 1996].

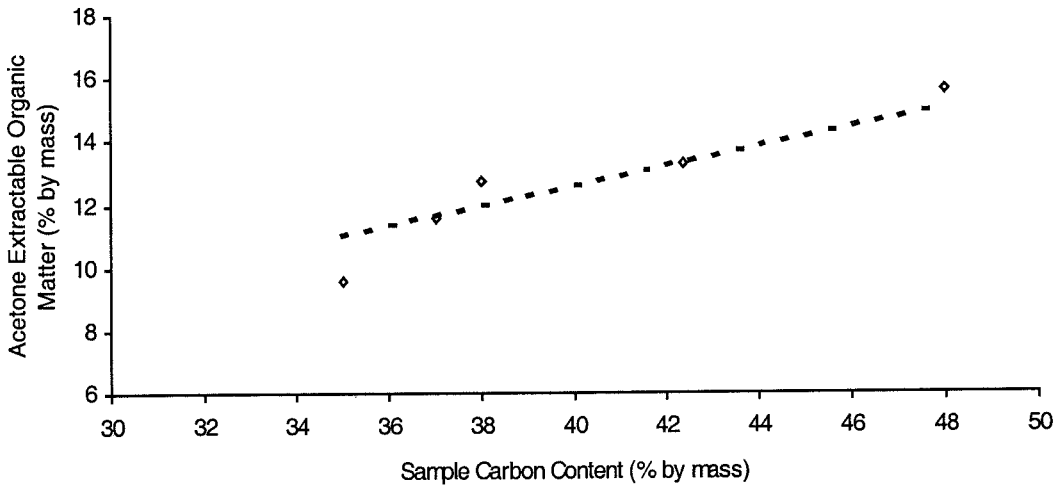
6.4.3 OC, and BC+EC Fractions

Accelerated solvent extraction of Tyne Tunnel samples has indicated a mean extractable organic content of 13.7±3.1% (1σ) by mass. TGA has indicated a mean carbonaceous fraction of the Tyne Tunnel samples of 39.5±6.8% (1σ) by mass.

Therefore the mean proportion of extractable OC of the mean carbonaceous fraction of the Tyne Tunnel samples is 32.2±7.4% (1σ), and the BC+EC fraction is assumed to represent the difference of 67.8±7.4% (1σ).

Chart 5.1 demonstrates a good agreement (r=+0.924) between extractable OC fraction and total carbon mass of each sample (determined by TGA), which corroborates the earlier supposition that composition commonalties exist between the Tyne Tunnel samples.

Chart 6.2 Relationship Between Sample Carbon Content and Extractable Organic Matter



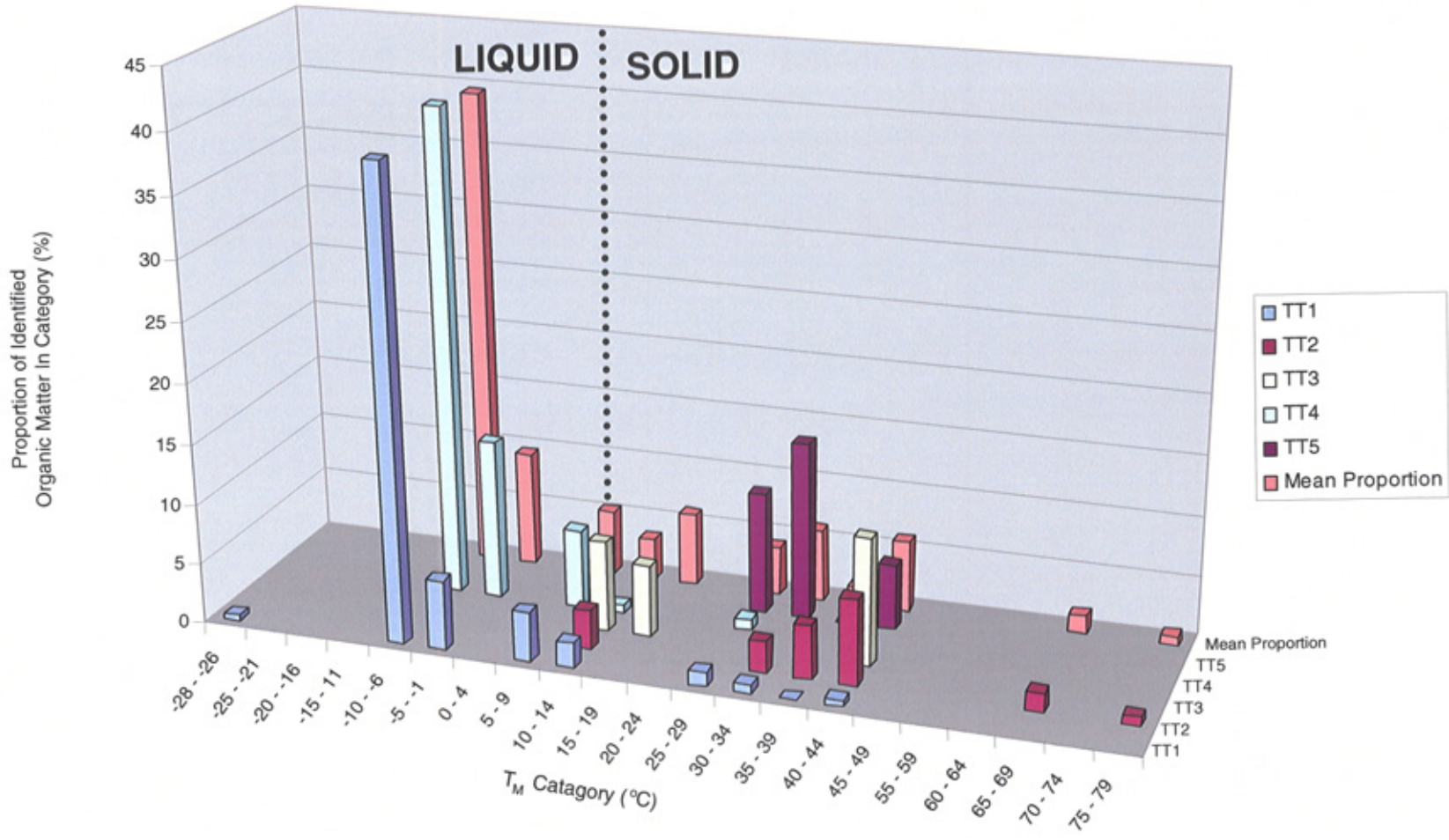
6.4.4 Physical State of OC

Table 6.6 indicates that the extracted OC of collected samples comprise mainly n-alkanes and alkylated alkanes, findings which agree with Eatough's (1995). However the samples contain a considerably lower proportion of oxygenated organic compounds than shown to exist within fine urban aerosol by Rogge et al. (1993), or total urban aerosol mass by Clain (1998). This may be due to:

- the seclusion of the sample CCA from the sunlit troposphere;
- samples collected by Clain and Eatough represent a wide range of aerosol types, and not just that associated with primary diesel emissions, and
- the mean size fraction of the sampled tunnel dust, which may be different to that collected by Clain and Rogge.

The physical state of these components at a range of temperatures can be visualised in Chart 6.3 below, which indicates the relative proportions of each organic compound by melting point categories of 5°C.

Chart 6.3 **Melting Points and Abundance of Principal Components of Extracted Organic Carbon**



NB The division between solid and liquid phase has been shown at the 10-14°C category

Melting point distributions indicate that approximately 70% of extracted organic matter is normally liquid at room temperature (25°C), and 59% at 5°C. This infers that a significant fraction of OC of diesel aerosol may undergo phase changes throughout the diurnal cycle, particularly in wintertime.

6.4.4.1 Occurrence of a Liquid Phase Upon Diesel CCA

Very little data is available regarding the surface area of BC+EC 'core components' of diesel aerosol. It has been acknowledged, however, that aerosol from hexane combustion has a large surface to mass ratio of the order of 100 m^{-2} g^{-1} for gas fixation, and approximately half this for liquid fixation (discussed in Section 2.4) [Schure et al., 1985; Smith et al., 1989]. Due to the scarcity of reliable data, these values have been adopted.

Assuming that the carbonaceous fraction of tunnel samples is representative of diesel aerosol, at a mean ambient temperature of 5°C, approximately 60% of OC associated with diesel aerosol is expected to be in a liquid state. Therefore, a theoretical diesel aerosol concentration of 0.5mg m^{-3} comprises:

1 0.34 mg m^{-3} BC+EC fraction, which provides a surface area for gas fixation of 0.034 m^{-2} m^{-3}, and 0.017m^{-2} m^{-3} for liquid fixation;

2 a mean OC fraction of 0.161 mg m^{-3};

3 an LOC fraction of 0.097 mg m^{-3}, with a mean RMM* of 175; and

4 an SOC fraction of 0.064 mg m^{-3}, with a mean RMM* of 254.

*factored by relative abundance of each compound.

It is important to note that although diesel aerosol is highly carbonaceous, the assumed diesel aerosol carbon content of 100% above in reality is not likely to occur.

The above leads to an LOC mean concentration of $3.34.x10^{17}$ molecules m^{-3}

and an SOC mean concentration of $2.58.x10^{17}$ molecules m^{-3}

Molecular Surface Area Coverage Potential

Estimation of mean molecular Surface Area Coverage Potential (SACP) of SOC and LOC fractions has been achieved using Hyperchem© Release 4 (Hypercube Inc.), using Polak-Ribiere conjugated geometry optimisation (RMS gradient of 0.1 kcal/Å mol).

A mean molecular SACP of the LOC fraction was estimated to be 50 $Å^2$, from the individual surface areas of the two main components – n-dodecane, and n-tridecane (factored by the relative abundance of each).

Similarly, mean molecular SACP of the SOC fraction was found to be 81 $Å^2$ from an average of molecular SACP's of heptadecane, hexadecane, octadecane, methylnonadecane, eicosane, and heneicosane (again, factored by the mean relative abundance of each).

BC+EC Surface Coverage by SOC

It has been assumed that SOC compounds will preferentially occupy BC+EC surface sites, by physical adsorption, and therefore the surface area measurement for gas adsorption has been used. The total SACP of the SOC fraction is therefore estimated to be 0.21 m^2, approximately 6 times greater than the estimated surface area of 0.5 mg of diesel aerosol. This confirms the existence of considerable organic multilayer formation upon the BC+EC surface of diesel surface, corroborating suggestions by earlier work [Berner et al., 1996; Smith and O'Dowd, 1996].

Physical adsorption is a competitive process, and preference towards surface sites of the adsorbent material occurs for those compounds demonstrating highest enthalpies of adsorption. As enthalpies of adsorption are, in general, related to the volatility of an adsorbate, the SACP of the SOF suggests the extent to which BTEX aromatics are physically adsorbed upon the EC+BC core surface of diesel CCA is negligible.

Surface Coverage of BC+EC by LOC

The total surface coverage potential of the LOC fraction is estimated to be 0.17 mm^2, which is approximately 10 times greater than the estimated available surface area (for liquid fixation) of diesel BC+EC fraction, within 0.5 mg diesel aerosol.

It is unlikely, considering the morphological diversity of combustion aerosol, that an LOC fraction would occur in a uniform film across the entire EC+BC core surface, and in areas, may occur to considerable depth. Such LOC coverage may further limit the availability of gas/liquid fixation sites by the blocking of pore structures, leading to greater depths of LOC upon the surface of the EC+BC core.

6.4.5 Volatility of OC Fraction Components

SPME analyte collection from sample headspaces has shown a wide range of volatile and semi-volatile compounds. Those, which have been satisfactorily identified, are presented in Table 6.7.

Although the approximate abundance of each species collected by the SPME fibre is not necessarily representative of their concentrations within the sample matrix, this preliminary study does appear to indicate that a greater fraction of volatile material exists in both tunnel samples, when compared to the TEOM and diesel soot samples.

The most volatile components, which have been satisfactorily identified, are isomers of trimethylbenzene.

6.4.5.1 Temperature dependence of BTEX Vapour Pressure

The following equation describes the temperature dependence of the vapour pressure of pure substances:

$$(y^*2.125) = ax + c$$

Where:

$y = \text{Log}_{10} P_{VAP}$ (mmHg). The factor of 2.125 converts y into units of Pa.

$x = 1/T$ (K) ; and

a and c are constants

Constants for the BTEX aromatics are presented in Appendix 3. Vapour pressures, calculated from the above relationship at a range of temperatures, are shown in Table 6.8 below, which includes values for 1,3,5-trimethyltoluene (mesitylene), the most volatile compound identified through SPME-GCMS analysis.

Table 6.8 Temperature Dependence of BTEX Vapour Pressure

Ambient Temp (K)	Vapour Pressure (P_{VAP}, Pa)						
	B [1]	Tol [2]	EB [1]	OX [3]	MX [2]	PX [3]	1,3,5 TMB [4]
270	2659.8	918.8	290.9	195.6	261.8	243.3	58.0
274	3403.4	1167.9	376.3	254.7	339.4	316.1	79.9
278	4324.6	1474.6	483.3	329.3	436.7	407.7	108.6
282	5458.3	1849.6	616.3	422.7	557.9	522.0	146.2
284	6845.2	2305.5	780.6	538.8	708.0	663.9	194.6
288	8531.7	2856.6	982.5	682.4	892.7	838.8	256.5
292	10571.1	3519.2	1229.0	858.7	1118.6	1053.2	334.9 / (351)[5]

[1] Ambrose et al., 1967 [2] Besley and Bottomly, 1974 [3] Osborne and Doulsin, 1974
[4] Forziati et al., 1949 (Antoine relationship)
[5] Daubert and Danner, 1989 (experimentally measured value)

The above table demonstrates that the BTEX aromatics collectively demonstrate a very wide range of vapour pressures, and indicates that the vapour pressures of benzene and toluene, even at lower temperatures, are much greater than those measured for compounds identified within the Tyne Tunnel samples. However, mesitylene was detected within a tunnel sample which had been collected at 290K,

therefore it is reasonable to propose that isomers of xylene may also be associated to some degree with the OC fraction of diesel aerosol at temperatures below 275K. This proposition assumes that isomers of xylene demonstrate a similar affinity for an LOC phase.

6.4.6 Estimation of Rate of Uptake of BTEX Aromatics by CCA

Although partitioning coefficients are widely used in binary phase systems, their application for description of the distribution of BTEX between gas and aerosol bound phases is limited because:

- BTEX aromatics are assumed to have an infinite solubility in the gas phase; and
- BTEX aromatics are assumed to have an infinite solubility in the LOC phase.

Therefore, numerical estimation of the process of uptake of the BTEX aromatics can be achieved by consideration of the rate determining processes:

- diffusion through the gas phase; and
- solubilisation into the LOC fraction.

6.4.6.1 Theoretical Rate of Uptake of Orthoxylene

A means of estimating the theoretical uptake rate of BTEX is through consideration of the collision frequency of BTEX with the LOC associated with diesel aerosol. This assumes that the LOC of diesel aerosol can be regarded as a single theoretical plane, the area of which has been calculated to be 1.3×10^{-3} m^2 m^{-3} (or m^{-1}) (for a diesel CCA concentration of 50 $\mu g m^{-3}$, with a 50% coverage of core components by LOC, and adopting a surface area for liquid fixation of $50 m^2 g^{-1}$).

In this example, the uptake rate of orthoxylene is explored at 1atm pressure and 278.2K temperature, at a concentration of 5ppb (or 1.33×10^{17} molecules m^{-3}).

The collision frequency (z) is defined as:

$$z = \frac{1}{4} n \bar{c}$$

Where n = molecules m^{-3} orthoxylene

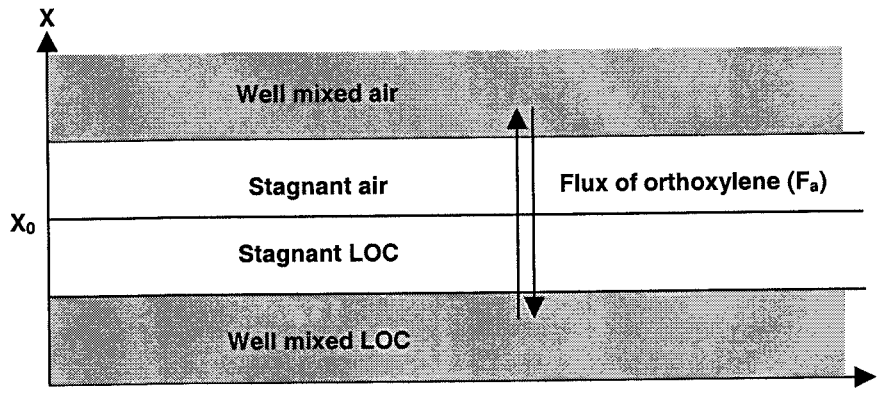
$\bar{c}$ = mean molecular speed, or $\left(\frac{8RT}{\pi m}\right)^{\frac{1}{2}}$ (ms^{-1})

$R = 8.31441\ JK^{-1}mol^{-1}$

m = RMM of orthoxylene $(gmol^{-1})$

Which leads to an orthoxylene collision frequency with an LOC phase of 7.856×10^{15} molecules $m^{-2}\ s^{-1}$. In this simple model, it is illustrated that uptake may be very rapid, however, the movement of orthoxylene molecules between air and LOC (or vice versa) will generally be controlled by the speed of passage between the boundary layers of each phase. The 'stagnant' boundary layer theory has been adopted to investigate this feature, as illustrated in Figure 6.3 [Liss and Slater, 1974].

Figure 6.3 Stagnant Boundary Layer Model for Air – LOC Phase



X_0 signifies the point of air – LOC contact
Adopted from Schwarzenbach et al., 1993

The rate of mass transfer (or flux, F_a) of orthoxylene across the boundary layers is defined by Fick's law:

$$F_a = -D_{BA} \frac{dC}{dX}$$

Where $\frac{dC}{dX}$ is the concentration gradient

D_{BA} is the diffusion coefficient of OX in air

Application of Fick's law has been applied assuming:

- a concentration of orthoxylene of 1.33×10^{17} molecules m^{-3} in air;
- a zero concentration of orthoxylene at the LOC surface;
- the diffusion coefficients of orthoxylene in air calculated using the Wilke and Lee model (Table 2.8) at 278K;
- an estimated diffusion layer thickness of 1μm [Skelland, 1985]; and
- that collisions occur with a theoretical plane of 1.3×10^{-3} m^2 m^{-3} (or m^{-1}).

This leads to an initial flux of across the boundary layer of 0.27 $\mu g s^{-1}$, which is very fast compared to, say, loss of orthoxylene through oxidation by hydroxyl radical. It is important to accept this is an initial rate. It is likely that the concentration gradient would reduce considerably over a short period of time due to saturation of the surface of the LOC with orthoxylene (the degree of mixing of absorbed BTEX into the bulk LOC phase is likely to be slow). It is envisaged that solubilised BTEX will return to the gas phase at a rate determined by the mole fraction of each aromatic within the LOC and the LOC temperature, if mixing of absorbed aromatics is sufficiently fast.

6.5 CONCLUSIONS

This chapter has discussed the likelihood of uptake of BTEX upon carbonaceous combustion aerosol, through absorption within a liquid organic phase.

There is considerable evidence from the experimental data that a significant fraction of carbonaceous aerosol occurs as a liquid at the normal range of UK atmospheric temperatures. Additional analysis of the OC fraction indicated that components, which may be considered volatile, are present within such aerosol.

This has been achieved using a relatively new technique of solid phase microextraction, which successfully provided a means of delivering volatile and semi-volatile organic analytes to the GCMS system 'solvent free'. However, the application of this technique illustrates that a solid support (or 'core' component), which is coated with a non-volatile organic liquid, may rapidly absorb organic gases from an atmosphere to which it is exposed, illustrating the postulated process of VOC uptake by CCA.

Calculated BTEX aromatic uptake rates indicate that this process is fast. It is likely that the degree of mixing of absorbed species from the interface of the LOC into the bulk LOC phase may be the rate determine step, and hence the viscosity of the LOC is likely to be critical.

Consideration of the available evidence leads to the conclusion that uptake of BTEX aromatics upon diesel aerosol by absorption into a LOC phase is very likely, and the extent to which this occurs is believed to depend upon:

- atmospheric temperature;
- mobility of LOC (i.e. the degree of mixing of the LOC and absorbed species)
- pressure of BTEX; and

- mass per unit volume of LOC.

Suggested experimental approaches for the development of this area are proposed in Chapter 8.

7 ISOLATED BOUNDARY LAYER ENVIRONMENT STUDY

7.1 INTRODUCTION

Chapter 5 has shown that through aggregation and transformation of large data sets to a diurnal time series, the differing boundary layer behaviour of the BTEX aromatics becomes apparent. Diurnal seasonality was noted for all ratio values (where both benzene and toluene were applied as reference aromatics).

It was concluded that three possibilities could account for a systematic nocturnal deviation of ratios from mean ratio values: reaction with ·OH, uptake onto CCA, or transport of air, bearing differing proportions of BTEX aromatics, to the study sites.

In order that these and other possibilities are confirmed or rejected, measurements of [BTEX] were collected within an 'isolated' environment (isolated in this context implies an atmosphere which is effectively isolated from the free boundary layer for a fixed fraction of the diurnal cycle).

The site selected for this study was a bus depot, which was closed overnight, during which time, the following processes were effectively ignored:

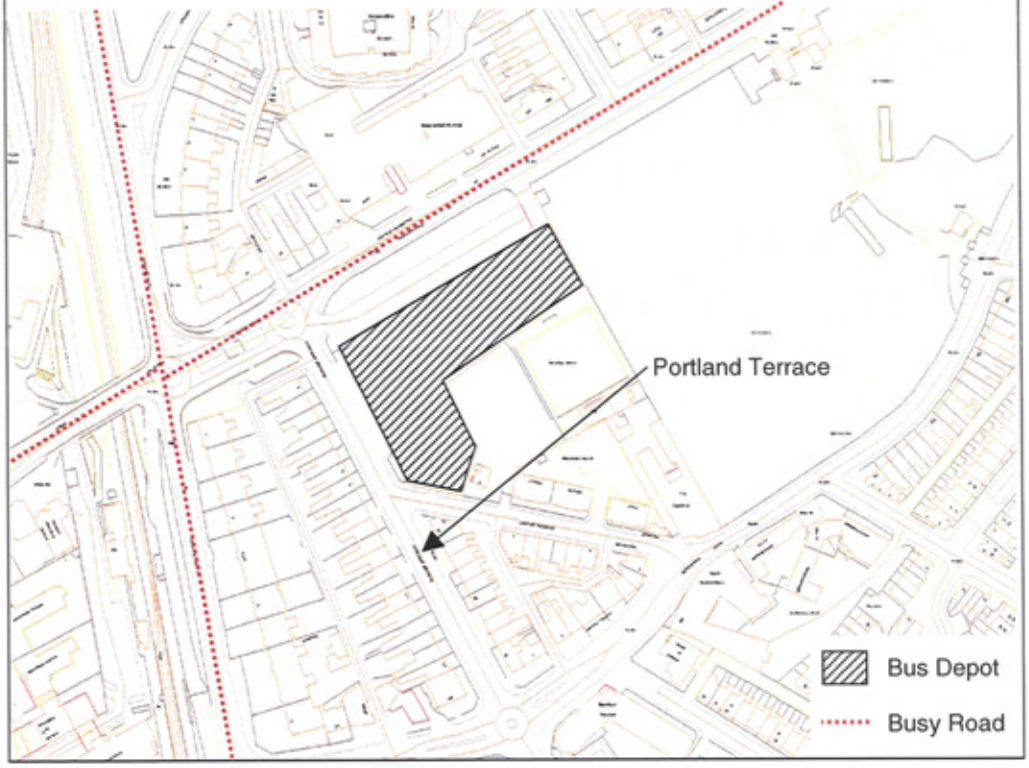
- systematic compositional change in road traffic (and consequent changes to individual BTEX emission rates) outside of the bus depot;
- significant mixing of 'isolated' air with other air accommodating a proportionally dissimilar composition of aromatic hydrocarbons (although is it recognised that a relatively small degree of mixing would take place), and transport of aromatic hydrocarbons from other, non-traffic related sources to the study site; and
- preferential precipitation scavenging of individual BTEX aromatics.

The site had an additional benefit – high levels of diesel CCA were present in the depot due to exhaust emissions from passenger buses, which provided an atmospheric environment where the hypothetical process of BTEX aromatic uptake into a liquid organic phase associated with diesel CCA could be explored.

7.2 DETAILS OF PORTLAND TERRACE BUS DEPOT

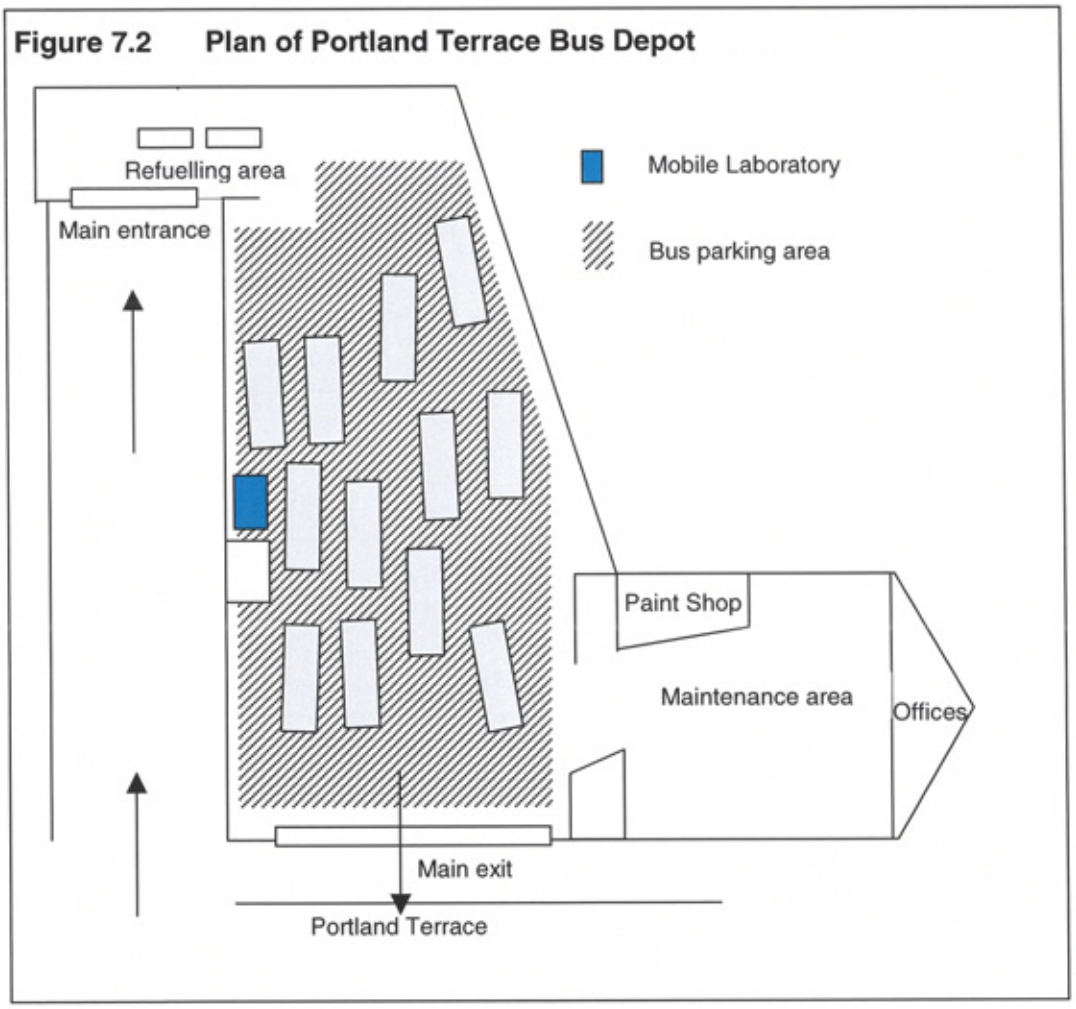
The site selected for this investigation was a large bus depot located to the west of the city centre of Newcastle upon Tyne (Figure 7.1). The bus depot was located at Portland Terrace, a relatively minor inner city road, which, at the time of this study, conveyed approximately 6000 vehicles per week-day, and 4000 vehicles per weekend-day.

Figure 7.1 Portland Terrace Bus Depot Location Plan



The depot served as an overnight parking garage for public transport buses, and included refuelling and maintenance areas, which may have been important sources of BTEX when in operation. Figure 7.2 and Plate A4.4 present the study location of the mobile laboratory within the depot. Fuel stored at this site comprised diesel only. All spraying of solvent based paints at this site was conducted behind a curtain, under local ventilation.

Figure 7.2 Plan of Portland Terrace Bus Depot



7.2.1 Bus Movement Schedule

At the time of this study, 24 two-decked buses operated from the Portland Terrace Station, of which 16 departed during 0530-0700 hours (the depot was opened at 0500 hours). As most of these buses were used by regional schools for carriage of school children, the majority returned to the station between 0900-1100 hours, and left the station for the second time at 1100-1300 hours. The majority of buses returned between 1600-1730 hours, after which time they were parked and left in the station overnight. The last bus to return reached the station before 0000 hours, after which time the depot was closed (isolated).

7.3 MEASUREMENT DETAILS

The site chosen for this study is summarised in Table 7.1 and described in detail below.

Table 7.1 Summary of Study Site

Site Name	Locality Description [2]	Measurement Dates	n[BTEX] / Cap (%)[3]	Other Measurements [4]
Northumbria Bus Depot, Portland Terrace	Urban background / isolated environment	18.01.00 – 04.02.00	749 / 96	WS, WD, AT, PM_{10}, SF[5], RF[6], RTF[7], BOS

[1] See Appendix 5 for locality definitions

[2] Mean number of half hourly [BTEX] measurements / mean data capture for BTEX. Data capture for individual BTEX aromatics is presented in Table 7.2

[3] WS =Wind Speed; WD =Wind Direction, AT = Air Temperature, SF = Solar Flux; RF = Rainfall; RTF = Road Traffic Flow; BOS = Bus Operation Schedule

[4] SF measurements collected by The University of Northumbria, Newcastle upon Tyne

[5] RF measurements collected by The Met. Office, Newcastle upon Tyne

[6] RTF measurements provided by the Division of PHEP, Newcastle City Council. Values presented in this chapter have been derived from manual traffic counts and factored using Global factors for Newcastle upon Tyne city centre

PM_{10} measurements were collected on only four days (19.01.00) due instrumental failure.

Additional measurements were provided by third parties (detailed in Table 3.3), which comprised hourly solar irradiance in Newcastle upon Tyne, hourly traffic flow at Portland Terrace (based upon a manual count, and globally factored for Newcastle City Centre), and daily mean air temperature.

7.4 RESULTS

7.4.1 Descriptive Statistics

Table 7.2 presents elementary statistics of measurements collected within the bus depot.

Table 7.2 Statistical Summary of Ground-Based Measurements

Parameter	B	Tol	EB	ΣPMX	OX	PM_{10}
No. Results (n)[1] / Cap (%)	688 / 95	723 / 98	722 / 98	723 / 98	723 / 98	196 / 27
Mean (ppb, or μgm^{-3} for PM_{10})	7.3	8.6	3.7	11.0	6.9	68.2
Mean Proportion [2] (%)	19.4	22.9	9.9	29.4	18.3	
Maximum (ppb, or μgm^{-3} for PM_{10})	40.8	48.3	31.0	112.9	25.6	900

[1] Number of measurements above limit of detection / % data capture

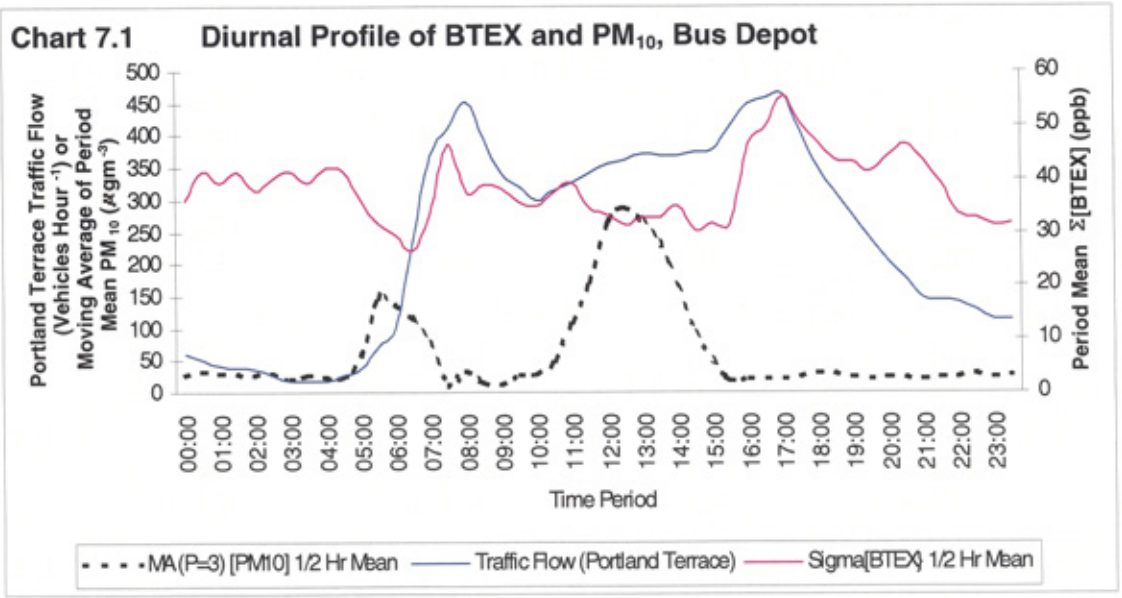
[2] Mean proportion of the total BTEX concentration, or $\alpha[BTEX] = \left(\frac{\bar{x}[BTEX]}{\bar{x}\Sigma[BTEX]} \right) x100$

The above table illustrates that the study site received high concentrations of all analytes, particularly PM_{10}, and measurements demonstrated a lower proportion of toluene compared to the study sites reported in Chapters 4 and 5. This may be a feature of the exhaust emissions from large diesel-fuelled buses. However, this suggestion is difficult to corroborate from available literature, as few studies have comprehensively reported upon VOC emissions from large diesel-fuelled vehicles.

This aside, similar proportions of other aromatic hydrocarbons have been recorded at other sites presented in this document, suggesting (considering all data) a significant proportion of BTEX reaching the mobile laboratory arrived from petrol fuelled road traffic outside of the bus depot.

Chart 7.1 presents the diurnal profile of [BTEX] and [PM_{10}] at the site, and includes estimated traffic flows at Portland Terrace. It is important to note that only 4 days of [PM_{10}] data were collected, all of which were midweek days. The emission profile of PM_{10} would most probably have been somewhat different over a weekend period. The PM_{10} data is presented as a 3 period moving average of half hourly means.

Chart 7.1 Diurnal Profile of BTEX and PM_{10}, Bus Depot



The above chart indicates a number of interesting features:

- that the concentration profile of Σ[BTEX] appears to positively correlate with road traffic flow, suggesting this is the principal source within the depot;
- that [PM_{10}] appears to be independent of both Σ[BTEX] and road traffic flow, however it does correlate highly with scheduled bus movement at the depot; and
- that Σ[BTEX] remains approximately constant between 0000 and 0430 hours. Rapid reduction of Σ[BTEX] at 0430-0600 hours is likely to have occurred through opening of the depot doors and consequent ventilation of the depot with traffic polluted air accommodating a lower absolute concentration of Σ[BTEX].

From these findings, the study location is considered an urban background site between 0430-0000 hours. The two periods of very high [PM_{10}] can be attributed almost exclusively to scheduled bus departure from the depot for collection of school children. It is interesting to note that Σ[BTEX] does not elevate during these periods. Considering the close proximity of the measurement site to bus exhaust emissions, this feature suggests that the concentration of BTEX aromatics within diesel fuelled vehicle exhaust emissions is very small, than compared to the BTEX aromatic concentration associated with petrol vehicle emissions.

7.4.1.1 Correlational Statistics

Table 7.3 presents correlational statistics for the study.

Table 7.3 [BTEX] and [PM_{10}] Correlation Matrix

	Total Study Period						Isolated Period (0000-0430)				
	Tol	EB	ΣPMX	OX	PM_{10}		Tol	EB	ΣPMX	OX
B	0.369	0.438	0.329	0.523	-0.010	**B**	-0.030	0.022	0.000	0.002
Tol		0.468	0.443	0.392	0.105	**Tol**		-0.021	-0.043	-0.056
EB			0.947	0.788	-0.155	**EB**			-0.006	-0.027
ΣPMX				0.697	-0.140	**ΣPMX**				0.012
OX					-0.140	**OX**				

The above table shows that a positive, however generally weak temporal intercorrelation exists between BTEX aromatics over the complete study period, suggesting a number of compositionally different sources had reached the study site. No intercorrelation between measurements collected overnight is noted, suggesting that absolute concentrations of individual BTEX may change, however at proportionally differing rates.

7.4.2 Frequency Distribution

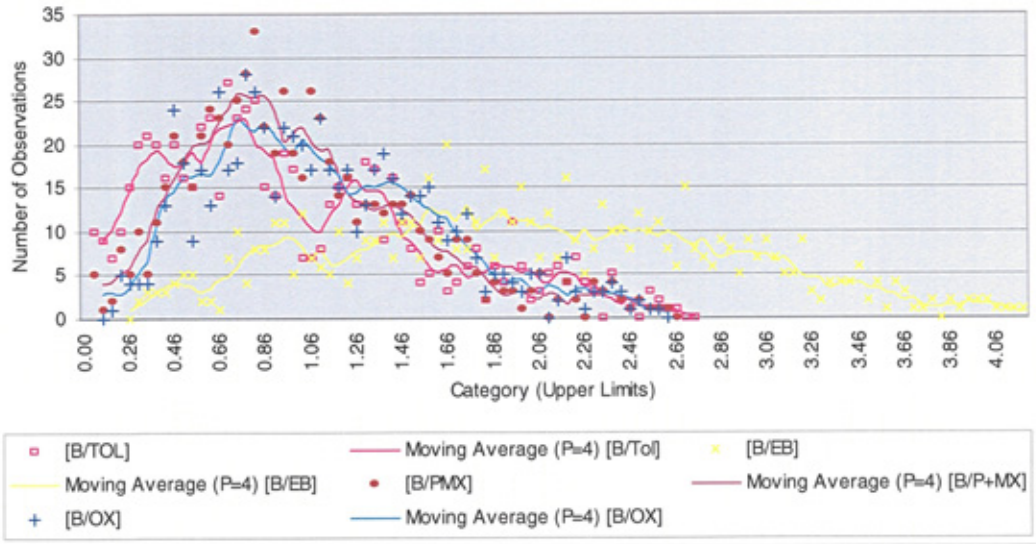
Chart 7.2 presents the distribution of all [BTEX] ratio values, and Table 7.4 presents distribution shape parameters for each aromatic hydrocarbon.

Table 7.4 Statistical Summary of $[B/Tol]_{(TOTAL)}$, $[B/EB]_{(TOTAL)}$, $[B/\Sigma PMX]_{(TOTAL)}$, and $[B/OX]_{(TOTAL)}$

	All Data Distribution Parameters			
	[B/T]	[B/EB]	[B/ΣPMX]	[B/OX]
Net Shape Distribution Parameters				
Skew	0.3	-0.2	0.5	0.1
Kurtosis	-1.2	-1.3	-1.2	-1.5
Mean±1σ	0.99 ± 0.60	2.15 ± 1.23	0.74 ± 0.37	1.14 ± 0.62
Isolation Period Distribution Parameters (0000-0430)				
Skew	1.1	1.0	0.9	1.3
Kurtosis	0.7	-0.4	0.8	-0.9
Mean±1σ	1.13 ± 0.63	2.32 ± 0.95	0.83 ± 0.40	1.23 ± 0.67

Mean ratio values during the isolated period demonstrate a systematic difference between those calculated for the entire study.

Chart 7.2 Frequency Distribution of $[B/Tol]_{(TOTAL)}$, $[B/EB]_{(TOTAL)}$, $[B/\Sigma PMX]_{(TOTAL)}$, and $[B/OX]_{(TOTAL)}$ for Bus Depot Site



The above chart does show a high degree of scatter in mean ratio values, however, skewness and kurtosis values indicate that the 'net' distribution, although broad, is essentially random. Night time distributions, however, do show a greater skew to the right, suggesting they are not completely independent variables.

7.4.3 Time Series Analysis

Ratio values, calculated between individual BTEX aromatics as described in Chapter 3, are presented as a net time series for the entire study day in Charts 7.3-7.6. A three-period moving average is presented for each aromatic ratio for visual clarity.

Table 7.5 presents a numerical expression of the mean data presented in Charts 7.3-7.6, as the mean relative standard ($\bar{x}\sigma'$) deviation of each period standard deviation (σ_{0000}, σ_{0030},....σ_{2330}) of concentration ratio values, i.e.:

$$\bar{x}\sigma'(\%) = 100\left(\frac{\bar{x}[B/TEX]_{(TOTAL)}}{\bar{x}_{(1\sigma_{0000},1\sigma_{0030},.....1\sigma_{2330})}}\right)$$

Table 7.5 Statistical Variance of Period Mean Ratio Values

	[B/T]	[B/EB]	[B/ΣPMX]	[B/OX]	Σ[BTEX]
Bus Station Site – All data					
($\bar{x}\sigma'$)	61.3	57.0	49.7	55.0	51.6
n'	14.3	14.3	14.3	14.3	14.3
1σ n'	1.2	1.2	1.2	1.2	1.2
Bus Station Site 0000-0430 hours					
($\bar{x}\sigma'$)	56.28	41.00	47.94	54.22	35.4
n'	15.5	15.5	15.5	15.5	15.5
1σ n'	0.5	0.5	0.5	0.5	0.5

1σ n' indicates the scatter of n measurements used for each period mean, over a 48 period cycle. Visual inspection indicates the distribution to be random

Values presented in Table 7.5 demonstrate a high degree of random variation, comparable to that calculated at Whitehaven (a study which comprised a similar number of [BTEX] measurements).

Chart 7.3 [B/Tol](TOTAL) Diurnal Time Series

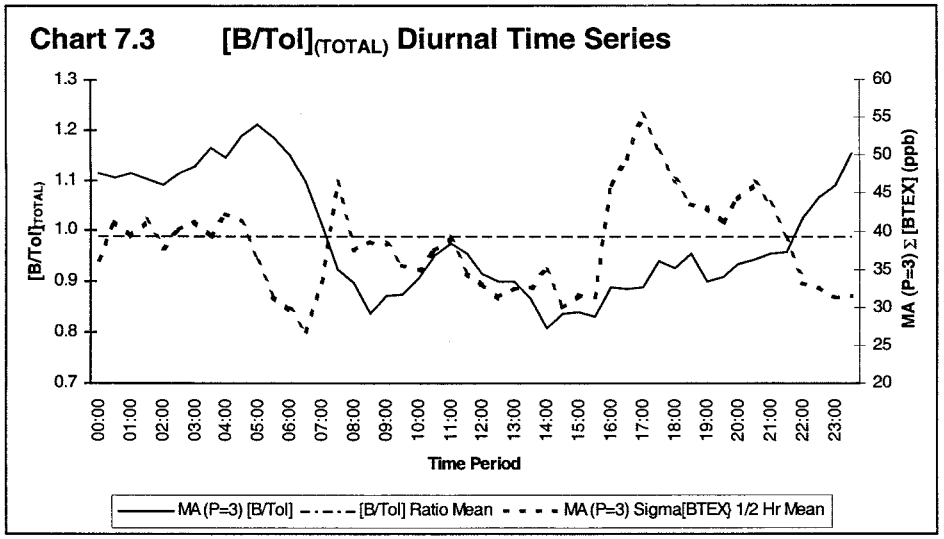


Chart 7.4 [B/EB](TOTAL) Diurnal Time Series

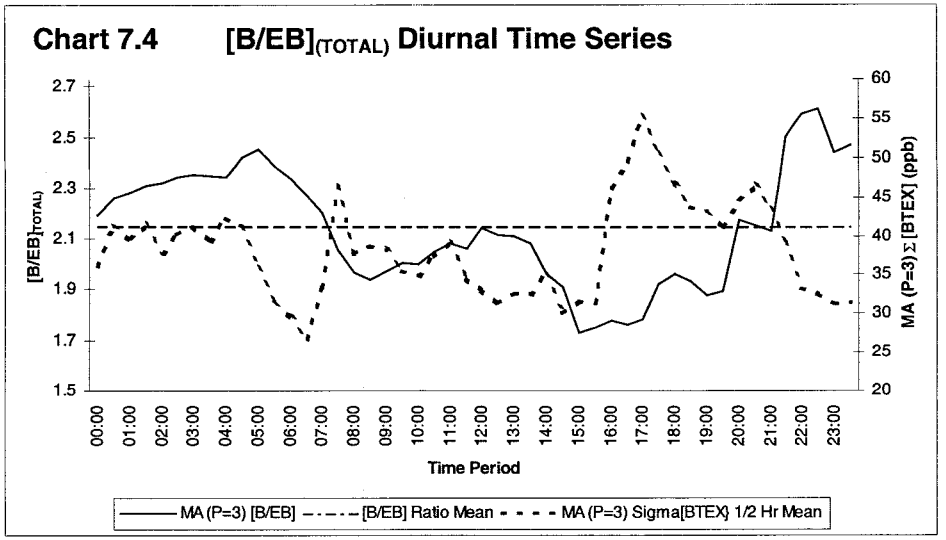


Chart 7.5 [B/ΣPMX](TOTAL) Diurnal Time Series

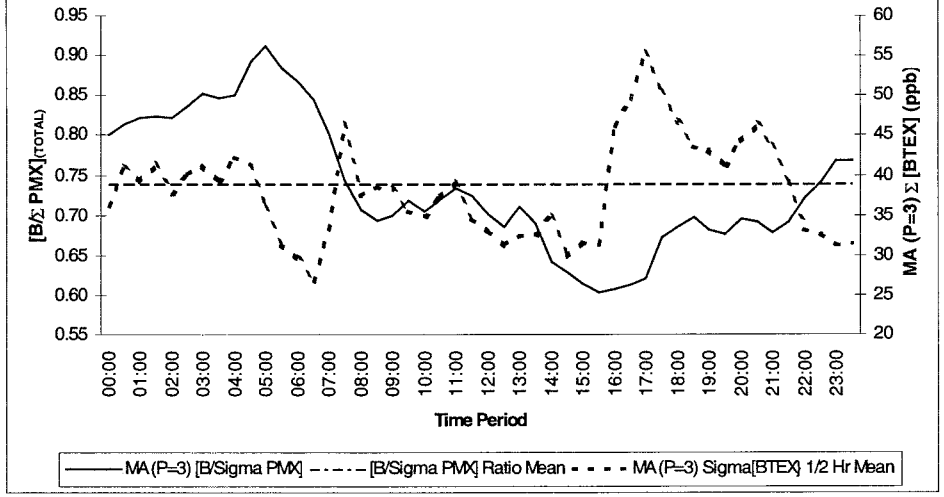
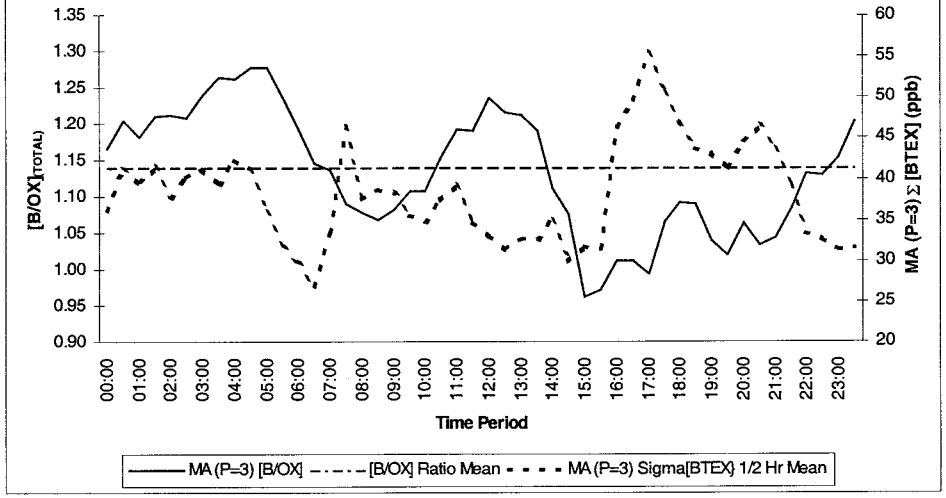


Chart 7.6 [B/OX](TOTAL) Diurnal Time Series



The time series above demonstrate that ratios between benzene (the reference aromatic) and other BTEX aromatics undergo a positive systematic deviation from mean ratio values between 0000-0400 hours. This departure from the mean value (between 0000 and 0430 hours) is similar to that noted for ratio values in the free boundary layer. In addition, differentiation of BTEX aromatic concentration appears to occur in a reasonably linear fashion. The return to the central tendency (0500-0700 hours) is fast compared to that noted for ratio values in the free boundary layer.

A lag of approximately 1-hour exists between the reversion of ratio values to below mean values, and the significant reduction of Σ[BTEX], features which occur between 0430 and 0630 hours. These profile changes can be explained by:

- rapid dispersion of BTEX when the depot doors were opened, which brought about reduction of the absolute concentrations of BTEX aromatics (i.e. Σ[BTEX]; and
- mixing of the bus depot atmosphere with urban air (which accommodated proportionally differing concentrations of BTEX aromatics). This process perturbed BTEX concentration ratio values only.

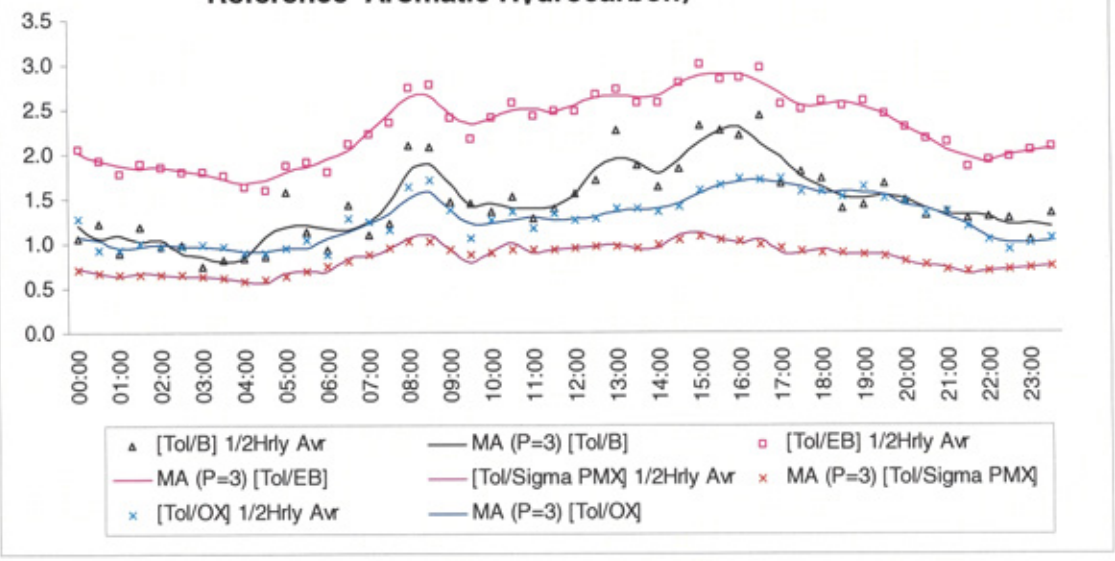
The lag between the profile features represents the difference in speeds of these processes.

Other changes to ratio values at other times, although not major systematic deviations, are likely to have arisen from mixing of emissions from diesel exhausts from buses, and petrol vehicle emissions from outside of the depot, which are believed to be compositionally dissimilar (Table 2.1).

The degree of random variability within the ratio values (noted in Table 7.5) prevents effective indexing of individual study days (to identify the degree of nocturnal differentiation of BTEX aromatics on each study day), even where a larger smoothing window is applied.

To demonstrate that the above seasonality apparent for each ratio profile is not a result of the variation of the absolute concentration of benzene only, ratios of the concentration of toluene with the other BTEX aromatics are presented below in Chart 7.7.

Chart 7.7 Net Time Series of BTEX Concentration Ratios (Toluene as 'Reference' Aromatic Hydrocarbon)



The chart above indicates that toluene does not show a 'zero slope' with other aromatic hydrocarbons. As with the free boundary layer, these profiles confirm that seasonality of aromatic hydrocarbons (using benzene as the reference compound) is not a result of the variation of the absolute concentration of benzene alone.

It is apparent from visual inspection of the chart that changes in the net absolute concentration of ΣPMX and OX closely resemble those of toluene, whereas ethylbenzene demonstrates significant variation.

Features of the above time series using both benzene and toluene as reference aromatics are expressed numerically in Table 7.6, and, for comparative purposes, rates of reaction with $\cdot OH$, and $NO_3\cdot$ are also included. Parameters in Table 7.6 are defined as followed:

- **(Ratio (0400+0430) – Ratio (0000-0030)/mean ratio value) * 100** This term describes the net degree of change in BTEX concentration ratios over the 'isolated period'. A negative value for this period indicates a negative slope on the time series profile.

- **The ratio of (Relative Saturated P_{VAP} at 278K) * (mean relative pressure of BTEX) for each aromatic** This term represents a ratio of 'CCA uptake index' values, which have been calculated from the saturated vapour pressure of each aromatic at 278K, and the pressure of each aromatic. This value is believed to represent the degree to which a species will be taken up by carbonaceous aerosol.

- **1/(Relative reaction rate with $\cdot NO_3$)** and **1/(Relative reaction rate with $\cdot OH$)** Kinetic rate values have been calculated using absolute concentrations of each aromatic recorded during the isolated period.

The data presented in the table on the following page demonstrates a number of features:

- that toluene is removed more effectively than all other BTEX aromatics during the isolated period;

- benzene is more 'persistent' than the other BTEX aromatics;

- that there is a lack of correlation between relative rates of reaction of BTEX with $\cdot OH$, and corresponding change of ratio values between 0000 and 0430 hours;

- no correlation is noted between relative rates of reaction of BTEX with $NO_3^{\cdot}$, and corresponding change of ratio values between 0000 and 0430 hours; and

- there appears to be a non linear relationship between the 'uptake index' and change in BTEX concentration ratios where both toluene and benzene are reference aromatics.

Table 7.6 Statistical Features of Time Series of BTEX Concentration Ratios

Parameter	Isolated Boundary Layer Ratio Values – Benzene as 'Reference' Aromatic			
	(B/Tol) [1]	(B/EB) [1]	(B/ΣPMX) [1]	(B/OX) [1]
Profile Feature Begin – End	0200-0430	0000-0430	0000-0430	0000-0430
(Ratio (0400+0430) – Ratio (0000-0030) / mean ratio value) * 100 (%)	+11.7	+14.6	+17.2	+14.7
The ratio of (relative Saturated P_{VAP} at 278K) * (mean relative pressure of BTEX) for each aromatic	3.5	19.9	7.4	15.3
1/(Relative reaction rate with NO_3)[2]	1.0	4.7	8.8	5.9
1/(Relative reaction rate with OH)	4.3 [3]	2.7 [3,4]	23.5 [3,5]	10.0 [3]
	Isolated Boundary Layer Ratio Values - Toluene as 'Reference' Aromatic			
Profile Feature Begin – End	0000-0430	0000-0430	0000-0430	0000-0430
(Ratio (0400+0430) – Ratio (0000-0030) / mean ratio value) * 100 (%)	-12.0	-32.5	-31.3	-33.1
The ratio of (relative Saturated P_{VAP} at 278K) * (mean relative pressure of BTEX) for each aromatic	0.3	5.7	2.1	4.4
1/(Relative reaction rate with NO_3)[2]	0.2	0.6	5.2	5.6
1/(Relative reaction rate with OH)	0.9 [3]	4.7 [3,4]	8.8 [3,5]	5.9 [3]

[1] Reaction rates presented are calculated using the mean concentration of each aromatic between 0000 and 0400

[2] Rate constants from Atkinson et al., 1984; Atkinson et al., 1989.

[3] Rate constants from Devolder, 1994

[4] Rate constant from Simpson, 1995

[5] Rate constant from Prinn et al., 1984

7.5 DISCUSSION

7.5.1 Statistical Features

7.5.1.1 Descriptive Statistics

During periods of high PM_{10} concentration (noted as two large peaks in the diurnal cycle), a subsequent elevation in BTEX concentration was not noted, suggesting diesel fuelled vehicle exhaust emissions accommodate very low concentrations of BTEX. However, the proportions of BTEX noted in the bus depot were dissimilar to those noted in the 'free' traffic-polluted boundary layer, which suggests that benzene was present within diesel exhaust emissions at a proportionally greater concentration than that of petrol exhaust emissions.

Exploration of the diurnal profile of BTEX aromatics and (a smaller sample of midweek) PM_{10} measurements indicate that during the isolated period (0000-0430 hours), BTEX and PM_{10} concentrations remained approximately constant, suggesting that the degree of mixing of isolated air with the free boundary layer was very small during this period.

7.5.1.2 Frequency Distribution

If the nocturnal differentiation of [BTEX] ratios is a feature of the free boundary layer (for example, through systematic traffic compositional variability) the frequency distribution of night time [BTEX] ratio values within an isolated environment (i.e. outside of the influence of such a process) would be expected to be normal. However, values presented in Table 7.4 demonstrate that [BTEX] ratios are dependent variables.

When the frequency distribution of ratio data for all time periods is considered, the variables demonstrate an approximately normal distribution. These distributions are generally broader than those calculated from measurements collected in the 'free'

traffic-polluted boundary layer. This may suggest a wider range of sources of BTEX aromatics reached the measurement site within the bus depot.

7.5.2 Time Series Analysis

Time series profiles of [BTEX] ratios (with benzene as the reference aromatic) indicate diurnal seasonality. The nocturnal profile resembles that calculated from measurements of BTEX aromatics in the free boundary layer (Chapter 5). Nocturnal deviation of ratio values from a mean ratio value (where benzene is the reference aromatic) is noted to reach a maximum at 0430 hours, and the slope becomes negative (i.e. reverses) at 0500 hours, coinciding exactly with the depot opening time. It is suggested that the reversing of ratio values towards their central tendency is a result of mixing of the isolated atmosphere with the free traffic-polluted boundary layer.

From these findings, it is postulated that similar reversals of concentration ratio values noted in the time series presented in Chapter 5, is a result of mixing of the 'nocturnal' boundary layer atmosphere with 'non-aged' BTEX emissions from emerging flows of road traffic, which begin at approximately 0530 hours.

The net time series of [BTEX] ratio values, using toluene as the reference aromatic, show significant seasonality for [Tol/EB] and [Tol/B] over the entire daily cycle.

Statistical analysis of both time series sets has suggested, through comparison of absolute net deviations of each ratio value with relative rates of reaction of aromatics in each ratio, that $NO_3^{\cdot}$ and $^{\cdot}OH$ are not responsible for nocturnal differentiation of [BTEX] values.

7.5.3 Evidence of Uptake of BTEX Aromatics Upon CCA

The 'uptake index' of each aromatic is an approximate means of representing the extent to which each aromatic may be absorbed within a liquid organic phase relative to other BTEX aromatics (i.e. not the uptake rate). These values demonstrate an reasonable non-linear relationship between the extent of deviation of concentration ratios calculated over the isolated period, using toluene as the reference aromatic (Chart 7.7).

Chart 7.7 Relationship Between Uptake Index and Relative Change of Ratio Values the During Isolated Period (0000 – 0430 hours) Using Toluene as the Reference Aromatic

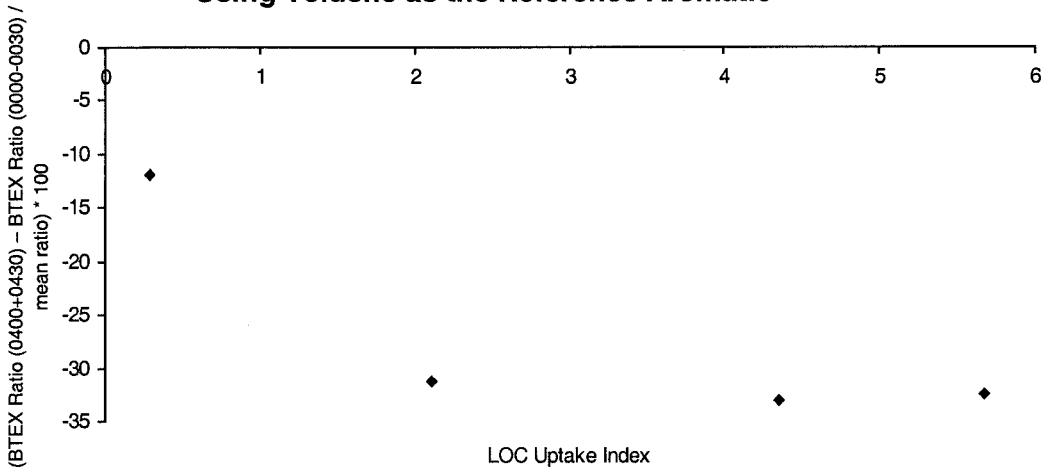
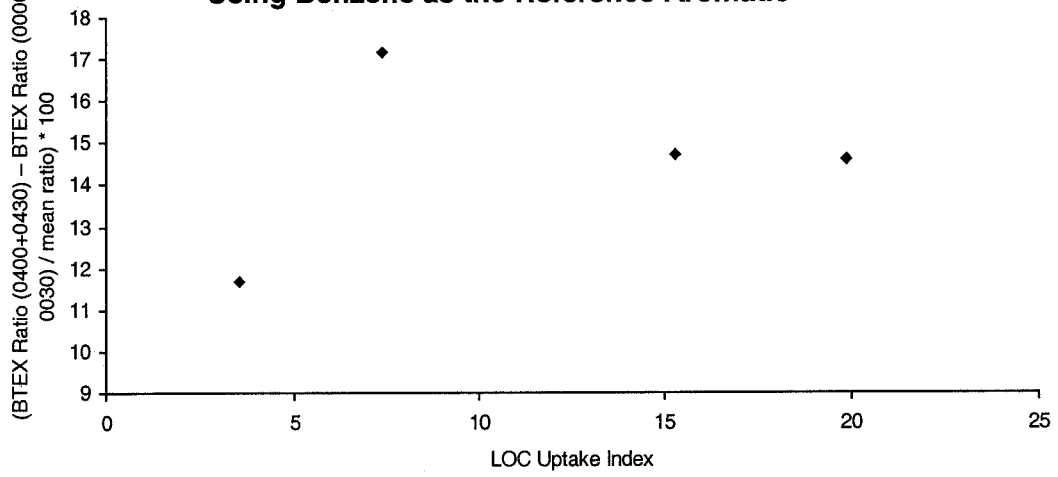


Chart 7.8 presents similar data where benzene has been applied as the reference aromatic.

These charts suggest that the volatility and pressure of each BTEX aromatic maybe related to the extent to which differentiation occurs for each ratio value between 0000 and 0430 hours. That is, BTEX aromatics with high partial pressure, and/or low volatility have tendency to be removed from the atmosphere at a greater rate than those of high volatility and/or low partial pressure.

Chart 7.8 **Relationship Between Uptake Index and Relative Change of Ratio Values During Isolated Period (0000 – 0430 hours) Using Benzene as the Reference Aromatic**



As noted in Chapter 6, hypothetically, an equilibrium between vapour and LOC bound phases of a volatile species is reached very rapidly, assuming mixing of absorbed organic species into the bulk liquid organic carbon phase is fast, and that uptake is diffusion controlled. Therefore, in order that this process may account for nocturnal differentiation of [BTEX] ratios, a shift in the position of equilibrium is required (and not a change in uptake rates). Within an isolated environment (such as that presented in this chapter), where the relative pressures of each gas remain unchanged, and the composition and concentration of diesel aerosol remains unchanged, the only critical, uncontrolled variable is atmospheric temperature.

The atmospheric temperature of the free boundary layer, recorded during a representative number of winter night time periods in Newcastle upon Tyne (measurements collected at the Northumberland Street site, December 1997, see Chapter 5) demonstrated approximately linear negative slopes between 0000 and 0430 hours (range of r values of between +0.78 and +0.96).

Therefore, if atmospheric temperature is a critical factor in the equilibrium position of gas particle distribution of BTEX aromatics, and the change in temperature is found to decrease in a linear manner between 0000 and 0430, then it would be expected that an approximately linear change in the position of equilibrium would occur over the isolated period.

Linear regression of [BTEX] ratio values with time period, between 0000 and 0430 hours, has demonstrated correlation coefficients of >+0.940. Linearity of differentiation was also noted within data collected in the free boundary layer at two separate sites.

7.6 CONCLUSIONS

This chapter has explored measurements of BTEX aromatics collected in an environment essentially isolated from the free boundary layer on each of every measurement day between 0000-0430 hours. During this period of the daily cycle, it has been shown that dispersion and mixing of the sampled 'isolated' atmosphere with the free boundary layer, does not occur to a significant degree.

Time series analysis has illustrated the occurrence of differentiation of individual [BTEX] concentrations, which has led to the rejection of the following postulated causal processes:

- systematic compositional change in road traffic;
- significant mixing of a sampled atmosphere with other air, accommodating a proportionally dissimilar composition of aromatic hydrocarbons; and
- transport of aromatic hydrocarbons from other sources.

Review of the net time series profiles during the isolated period, where either toluene or benzene was applied as a reference aromatic, showed no correlation to kinetic rates of reaction of BTEX aromatics with $\cdot OH$ or $NO_3\cdot$ free radical species. The change in aromatic concentration ratios with time was found to be approximately linear during the isolated period at the bus depot site, agreeing with findings from both study sites presented in Chapter 5.

Therefore, the nocturnal atmospheric temperature profile assists in the rejection of the hypothesis that a tropospheric reaction causes differentiation of individual [BTEX] aromatics. This is because the rate of [BTEX] differentiation between 0000 and 0430 hours would be expected to be non-linear with time if a tropospheric reaction was the

single cause, due to the reduction of atmospheric temperature (and hence reaction rate) over the isolated period.

Review of the linearity of differentiation of individual [BTEX] noted at this site, Northumberland Street and Whitehaven Town Centre sites, suggests that atmospheric temperature, the only meteorological parameter to demonstrate a nocturnal linear change with daily seasonality, is related to individual [BTEX] differentiation.

The available evidence serves to support the supposition that a physical process, which is related to atmospheric temperature, volatility of individual BTEX aromatics, and pressures of individual BTEX aromatics, govern the nocturnal differentiation of BTEX aromatics.

8 CONCLUSIONS AND RECOMMENDATIONS

8.1 CONCLUSIONS

This study has explored the relative behaviour of BTEX aromatics within urban, suburban, and isolated environments, with the aim of exploring their relative removal rates by processes other than their tropospheric oxidation by hydroxyl radical.

The Sunderland City Centre study has indicated that near to road traffic, proportional concentrations of BTEX aromatics demonstrate a very high degree of temporal consistency. In addition, studies within the free boundary layer have demonstrated that aggregated ratios of aromatic hydrocarbons provide a means of exploring the relative behaviour of BTEX over a daily cycle, features which are not apparent within time series of absolute concentrations of these compounds.

The 'shape' parameterisation of frequency distributions of such ratio values has proven to be a useful tool for indicating the degree of systematic and random variation in ratio value data sets. In addition, time series analysis of such ratio values has provided a means of visualising the relative behaviour of individual BTEX aromatics over a net daily cycle.

BTEX aromatics have been shown to demonstrate interesting wintertime nocturnal behaviour. No widely accepted process can account for such behaviour. A number of postulated processes had been proposed upon the findings of studies within the free boundary layer, which were explored through measurements of BTEX within an environment which was effectively isolated between 0000 and 0430 hours.

Although no single cause can be definitively determined, through processes of elimination, it can be concluded with a good degree of certainty that the following processes or features were not responsible for differentiation of BTEX concentration:

- systematic traffic compositional variability (and therefore source compositional variability) over night time periods;
- the influence of calendar events (i.e. weekends, holidays etc) over days when differentiation was found to occur most prominently;
- transport of BTEX aromatics from other areas accommodating a differing proportion of each aromatic (perhaps by extensive photochemical ageing of a parcel of air away from a measurement site);
- reaction of BTEX aromatics with nitrate radicals; and
- night time ·OH radical generation and corresponding reaction with BTEX aromatics.

The process of uptake of an organic gas by atmospheric aerosol is a well-documented process for many SVOC species. However, the absorption of a gas within a liquid organic layer, which is associated with carbonaceous aerosol has been postulated as possible cause of differentiation of BTEX aromatics (although no convincing evidence emerged from measurements of BTEX aromatics within the free boundary layer, this process could not be discounted).

This research considered the role of diesel aerosol in the fate of BTEX aromatics, by characterising settled diesel aerosol collected from a road tunnel. This work concluded that there is considerable evidence, from the available experimental data, that a significant fraction of carbonaceous aerosol occurs as a liquid at the normal range UK atmospheric temperatures.

It was also concluded that compounds were found to be associated with such aerosol that exhibited comparable volatility to isomers of xylene.

Hypothetical BTEX aromatic uptake rates were found to be fast, and it was suggested that the degree of mixing of absorbed species from the interface of the LOC into the bulk LOC phase may represent the rate determine step of uptake.

This work indicated that the following factors govern the extent of uptake:

- atmospheric temperature;
- mobility of LOC (i.e. the degree of mixing of the LOC and absorbed species)
- pressure of BTEX; and
- mass per unit volume of LOC.

Review of the linearity of differentiation of individual [BTEX] which was recorded at both an isolated environment and the free boundary layer, suggests that atmospheric temperature, the only meteorological parameter to demonstrate a nocturnal linear change with daily seasonality, is related to individual [BTEX] differentiation.

In addition, review of the net time series profiles collected within a nocturnal isolated environment indicated that the volatility of individual BTEX aromatics and pressure of individual BTEX was related to the extent of differentiation of BTEX over the nocturnal period.

The available experimental and theoretical evidence collected in this research serves to support the supposition that a physical process, which is related to atmospheric temperature, volatility of individual BTEX aromatics, and pressures of individual BTEX aromatics, governs nocturnal differentiation of BTEX aromatics.

8.2 RECOMMENDATIONS FOR FURTHER WORK

A number of recommendations for further work are presented below.

8.2.1 Atmospheric Studies

- One of the difficulties associate with deconvolution of systematic trends within BTEX measurements is random variation or noise. Significant improvement in the confidence of systematic deviation would be gained if larger data sets were collected, or, preferentially, data was gathered at a greater temporal resolution (with similar detection limits to those reported in this research);
- All experimentally determined removal rates presented within this document are relative values. Concurrent measurement of a chemically inert tropospheric species could yield accurate absolute removal rates, allowing comparison of, say, nocturnal sink mechanisms with hydroxyl radical oxidation;
- A longer study of a well mixed, indoor environment with high BTEX concentration would be interesting, particularly where high temporal resolution of measurements were performed during periods of large climatic variability;
- Photolysis of O_3 in the presence of water vapour is a major source of ·OH radicals [Atkinson, 2000]. Although humidity has received little attention, this research could be furthered by consideration of the role of sunlight, temperature and humidity in the relative rates of removal of BTEX aromatics by investigation of their concentrations in the sunlit troposphere.

8.2.2 Diesel Aerosol Studies

Although Chapter 6 has provided substantial evidence for uptake of BTEX by an LOC associated with diesel aerosol, the study only purports to exploratory work and requires further investigation. Proposed areas of exploration include:

- Development of the methodological approach of SPME-GCMS analysis for further qualitative tests to detect the presence of BTEX associated with diesel aerosol
- Although somewhat ambitious, a means of exploring uptake rates at a range of temperature could be achieved by exposing samples of diesel aerosol to atmospheres accommodating known concentrations of BTEX aromatics. Exposure at a range of temperatures may lead to controlled differentiation of individual concentrations of BTEX as noted within this study.
- It is accepted that physical adsorption is important in the gas particle distribution of PAHs and other SVOCs. Investigation of the occurrence and extent of the distribution of a species between a vapour phase and an LOC bound phase (by absorption) is very worthy of attention, as this may dictate to which aerosol types, SVOC pollutants may preferentially associate.

APPENDICES

APPENDIX 1 NATIONAL AIR QUALITY STRATEGY OVERVIEW

A1.1 INTRODUCTION

The United Kingdom's National Air Quality Strategy (NAQS), the first of its kind in Europe, was published in March 1997. It fulfilled the requirement under the Environment Act 1995 for a national strategy setting policies for the management of ambient air quality throughout the UK.

The key objective of the strategy was the setting of health based air quality standards for eight key pollutants: benzene, 1,3-butadiene, carbon monoxide (CO), lead, nitrogen dioxide (NO_2), Ozone (O_3), Particles (PM_{10}) and sulphur dioxide (SO_2). Originally a target date of 2005 was set for their achievement.

A revised version of the strategy was published January 2000, based on the recommendations of the strategy review which was carried out during 1998. Its recommendations, contained in a consultation document published in January 1999, include a reduction of the limit for particles and the target dates for fulfilling the objectives for benzene, 1,3-butadiene and carbon monoxide have been brought forward two years. The review also defines acceptable levels for particles and sulphur dioxide during a 24 hour period.

Where one or more of the air quality objectives is not likely to be met by the target date, the local authority is bound to declare an Air Quality Management Area (AQMA) and prepare and implement a programme of remedial actions.

Central to the LAQM is the management of transport, which is recognised as a substantial contributor to air pollution, especially in urban areas (Chapter 2.1). The main outdoor sources of VOCs have been identified as petrol engine vehicle exhausts and the distribution and uncontrolled emissions from petrol station forecourts.

The development and implementation of local authority transport planning is managed by the DETR through the annual Transport Policies and Programme (TPP), whereby local authorities bid for resources to support their transport policies. An advice note circulated in June 1997 encouraged local authorities to include measures in TPP bids which "stimulate innovation, enhance quality and choice in the provision of public transport".

It would appear that the potential damage to local public relations as a result of the declaration of an AQMA has yet to sink in. The subsequent programme of remedial actions is also likely to leave a bitter pill for local inhabitants to swallow and could include limitation of traffic flow, partial or complete closure of traffic routes, restriction of vehicles based on fuel type and the regulation of delivery vehicle movement.

A1.2 AIR QUALITY STANDARDS AND OBJECTIVE STANDARDS

The standards apply in non-occupational, near-ground level, outdoor locations where people might reasonably be expected to be exposed over the relevant averaging period and are based on recommendations of the Expert Panel on Air Quality Standards (EPAQS).

Table A1.1 Air Quality Standards and Objective Standards				
Pollutant	**Current Standard**		**Objective to be achieved by 2005**	**Proposals for amendments to the NAQS objectives**
Species	**Standard**	**Measured As**	**Objective**	**Measured As**
Benzene	5 ppb	running annual mean	5 ppb	5 ppb (16.2 μgm^{-3}) mean by 31.12.2003; indicative level of 1 ppb (3.2 μgm^{-3}) by 31.12.2005
1,3-Butadiene	1ppb	running annual mean	1 ppb	1 ppb (3.2 μgm^{-3}) by 31.12.2003
Carbon monoxide	10 ppm	running 8-hour mean	10 ppm	10 ppm (11.65 mgm^{-3}) by 31.12.2003
Lead	0.5 μgm^{-3}	annual mean	0.5 μgm^{-3}	0.5 μgm^{-3} by 31.12.2004 0.25 μgm^{-3} by 31.12.2008
Nitrogen dioxide	150 ppb	1 hour mean	150 ppb, hourly mean*	104.6 ppb (200 μgm^{-3}) by 31.12.2005 (maximum of 18 exceedences per year)
	21 ppb	annual mean	21 ppb, annual mean	21 ppb (40 μgm^{-3}) retained as provisional objective for 31.12.2005. Annual national objective for the protection of vegetation of 15.7 ppb (30 μgm^{-3}) for 31.12.2000.
Ozone	50 ppb	running 8-hour mean	50 ppb, measured as the 97th percentile of daily maximum 8 hour running mean*, (equivalent to 10 exceedences per year)	50 ppb (100 μgm^{-3}) retained as indicative level for 31.12.2005.
Particles (PM_{10})	50 μgm^{-3}	running 24 hour mean[1],	50 μgm^{-3}, measured as the 99th of daily maximum running 24 hour mean (equivalent to 4 exceedences per year)	New annual objective of 40 μgm^{-3} and 24 hour objective of 50 μgm^{-3} (maximum of 35 exceedences for 31.12.2004. 50 μgm^{-3}, as 99th percentile of daily maximum running 24 hour means to be retained as indicative level for 31.12.2005. New indicative annual level of 20 μgm^{-3} and 24 hour level of 50 μgm^{-3}, (maximum of 7 exceedences) for 31.12.2009.
Sulphur dioxide	100 ppb	15 minute mean	100 ppb, measured as the 99.9th percentile of 15 minute mean*, (equivalent to exceedences of 35 periods of 15 minutes per year)	100ppb (267 μgm^{-3}) as 99th percentile of 15 minute means adopted as firm objective for 31.12.2005. New 1 hour objective of 131ppb (350 μgm^{-3}), not to be exceeded more than 24 times per year, and 24 hour objective of 46.8 ppb (125 μgm^{-3}), not to be exceeded more than 3 times per year, for 31.12.2004. New national annual and winter objectives for the protection of ecosystems of 7ppb (20 μgm^{-3}) for 31.12.2000.
[1] objectives which are regarded as provisional in the Strategy				

A1.3 AUN SITES

A brief description of AUN Sites, data from which has been presented in this document, are presented below.

A1.3.1 Leeds

Site Address: Leeds Environmental Department, Potternewton Area Office, Blake Grove.

OS Grid Reference: SE307367

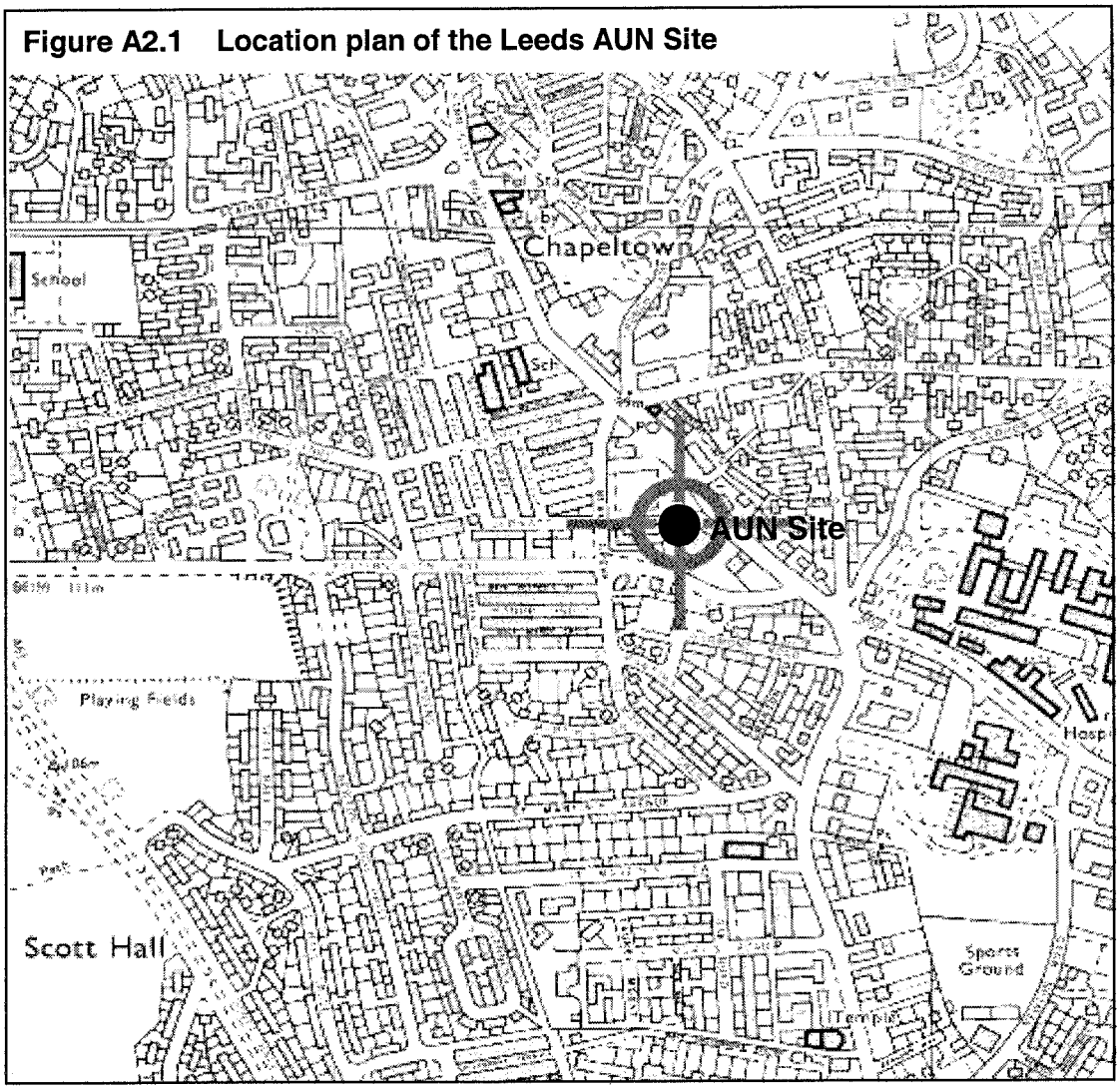
Site Type: Urban Background

Start Date: 13/01/95

Pollutants Measured: Hydrocarbons

Figure A2.1 illustrates the location of the AUN site.

Figure A2.1 Location plan of the Leeds AUN Site



A1.3.2 Middlesborough

Site Address: Breckon Hill School, Breckon Hill Road, Middlesbrough.

OS Grid Reference: NZ505194

Site Type: Urban Industrial

Start Date: 01/01/93

Pollutants Measured: O_3,CO,SO_2,PM_{10},NOx, Hydrocarbons

Figure A2.2 presents a location plan of the AUN site.

Figure A2.2 Location plan of the Middlesborough AUN Site

APPENDIX 2 SUMMARY OF ANALYTICAL TECHNIQUES ASSOCIATED WITH THIRD PARTY MEASUREMENTS

A2.1 DIFFERENTIAL OPTICAL ABSORBANCE SPECTROSCOPY (DOAS)

A2.1.1 Introduction

DOAS has been found to be most useful for the unattended analysis of part per billion by volume levels of organic and inorganic gas phase pollutants [Platt et al., 1979].

A2.1.2 Technique

A light source is placed typically 200-1500 meters from the receiving point. The light crossing this path (the sample atmosphere) is focused by a parabolic mirror in the receiver, the focused light being delivered to the entrance slit of the spectrograph [Platt and Perner, 1988].

The grating separates the light into different wavelengths, which are projected across the exit slit. A small part of the spectrum is scanned only at one time by means of a slotted disc device, a thin metal disc, which has many radially etched slots. The analyser only uses one slot at a time as the exit slit. A photomultiplier tube (PMT) then amplifies the light, and the recorded signals are sent to a computer and stored. By scanning and storing several hundred 'snapshots' of the spectrum at intervals of ~ 0.2 nm, it is possible to reconstruct the absorption spectrum over a region of 20-40 nm. By sequential subtraction, it is possible to determine the spectral absorption contribution of each VOC.

For some time the technique was restricted to the analysis of only one VOC, formaldehyde, but recently DOAS has been extended to benzene, toluene and

isomers of xylene, but has demonstrated questionable performance, as described in Section 2.1 [Grant et al, 1992; Brocco et al, 1992].

A2.1.3 Calibration and Performance

Calibration is achieved by placing a quartz windowed glass cell upon the receiving telescope, through which calibrant gases are passed.

Representative analytical performance details are provided in Table A3.1.

Chart A2.1 Analytical Performance of Opsis Differential Optical Absorption Spectroscopy

Determinant	Path Length (m)	Limit of Detection (μgm^{-3})	Precision (%)	Accuracy (%)
Nitrogen Dioxide	184	3	16	10
	1099	1	11	10
Ozone	184	7	8	8
	1099	5	6	8
Sulphur Dioxide	184	7	26	10
	1099	5	18	10

Values from Stevens and Vossler (1991)

A2.2 METEOROLOGICAL DATA

The following information was provided by The Meteorological Office.

A2.2.1 Hourly Rainfall Measurement

The tipping bucket rain-gauge has two identical buckets which pivot so that each can be filled in turn by rainfall from the gauge collector funnel. When a bucket is full its weight causes it to tip and a switch is closed, the other bucket then takes its place under the funnel spout and starts to fill. Reliable and robust gauges are available which, when calibrated correctly, provide satisfactory readings of hourly and daily

rainfall totals. The available resolution, 0.1 or 0.2 mm, provides measurements of rainfall rate and the times for the stop and start of rainfall. However, the timing and measurement of the intensity of very light rain or drizzle will be of limited accuracy.

A2.2.1.1 Performance

Measurement Range	0 to 999 mm
Resolution	0.2 mm
Accuracy	0.2mm <4mm, ±5%;
	>4mm, ±4%.

A2.2.2 Air Temperature

Measured by an electrical resistance thermometer (ERT). The sensor is encapsulated in a stainless steel sheath, which provides robustness and limits the speed of thermal response, and is protected by a thermometer screen from sunlight and rainfall.

A2.2.2.1 Analytical Performance

Measurement Range	-30 °C to +40 °C
Sensitivity	0.1 ° C
Accuracy	±0.2 ° C

A2.2.3 Wind

Wind measurements, both at the ML and by the Met Office, were performed by an anemometer and wind vane. Wind speed is usually measured by the rotation of a cup anemometer or propeller system which provides a continuous output from an

electrical generator. Wind direction is measured using a balanced vane whose rotation is sensed by potentiometer or relay closures.

A2.2.3.1 Performance

Wind speed:	Range	0 to 150 knots
	Resolution	0.1 knot
	Accuracy	±1 knot or 5%
Wind direction:	Range	10 to 360 degrees
	Resolution	1 degree
	Accuracy	±10 degrees

A2.2.4 Radiation

Measured collected by the University of Northumbria were performed by radiometer. In this type of instrument radiation falls on a thermopile which consists of a set of thermocouples with hot junctions exposed to the light and cold junctions hidden within the unit.

A2.2.4.1 Performance

Global radiation	Range	0 to 1.2 kWm^{-2}
	Resolution	1 Wm^{-2}
	Accuracy	±5%

APPENDIX 3 PHYSICAL AND CHEMICAL DATA FOR BTEX

Table A3.1 presents a compilation of physical data presented within this document.

Chart A3.1 BTEX Physical and Chemical Properties

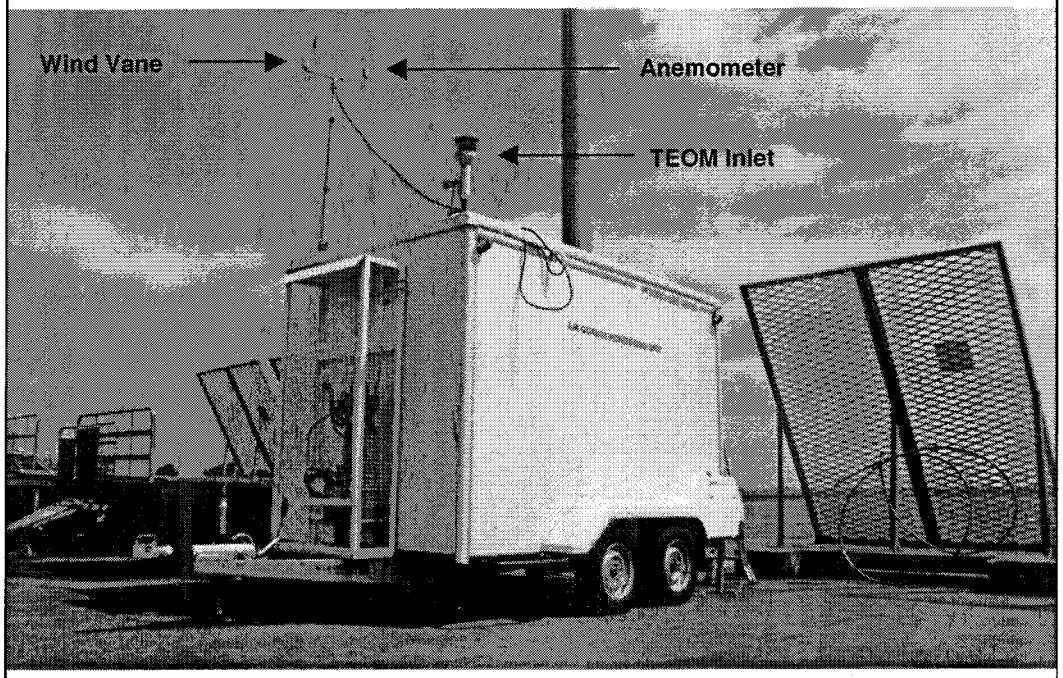
PARAMETER	Benzene	Toluene	Ethylbenzene	Orthoxylene	Metaxylene	Paraxylene
Physical Properties						
RMM ($g\ mol^{-1}$)	78.11	92.14	106.17	106.17	106.17	106.17
Boiling point (K)	353.3	383.8	409.4	417.6	412.3	411.5
Melting point (K)	278.4	178.2	175.2	248.0	225.3	259.9
Liquid density (gl^{-1}, 293.2K)	0.8765	0.8669	0.8670	0.8611	0.8642	0.8802
Solubility in Water (g $100ml^{-1}$ at 293.2K)	0.18	0.05	0.02	<0.01	<0.01	<0.01
Vapour Density (gm^{-3}, 0°C)	3.49	4.11	4.74	4.74	4.74	4.74
Vapour Pressure Temperature dependence where: $y = \log P$ (mmHg) and $x = 1/T(K)$	y=-2038.7x + 8.7409	y=-1984.2x + 8.08	y=-2129x + 8.109	y=-2186.1x + 8.1449	y=-2164.8x + 8.1621	y=-2145.5x + 8.1235
Henry's Law Constant, H (Pa Mol^{-1} Atm, 298K) [1]	0.18	0.15	0.12	0.19	0.13	0.13
Temperature Dependence of K_H [1]	3200	3000	5000	3200	3500	3300
Wilke and Lee diffusion Coefficient D_{BA} ($cm^2\ S^{-1} \times 10^{-2}$, 298.2K and 1 Atm) [2]	9.61	8.52	7.71	7.70	7.69	7.71
Refractive Index (298.2K)	1.498	1.494	1.493	1.506	1.495	1.493

[1] **Ashworth et al., 1988** [2] **Wilke and Lee, 1955**

APPENDIX 4 PLATES

Plates A4.1-4 present images of the mobile laboratory.

Plates A4.1-4.2 Mobile Laboratory Exterior



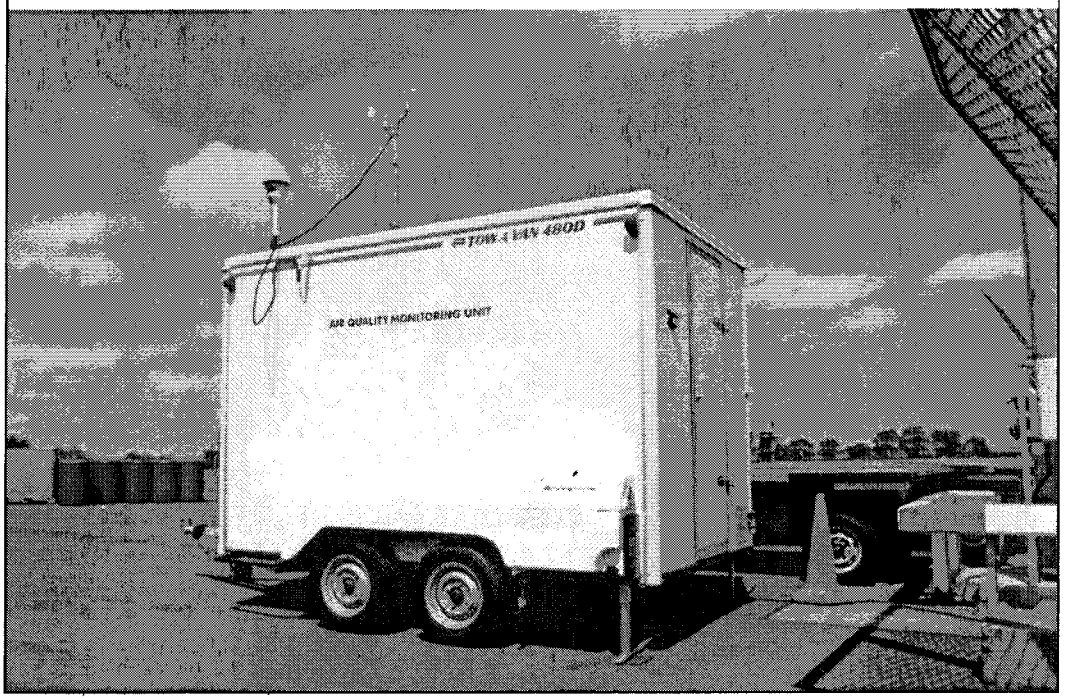
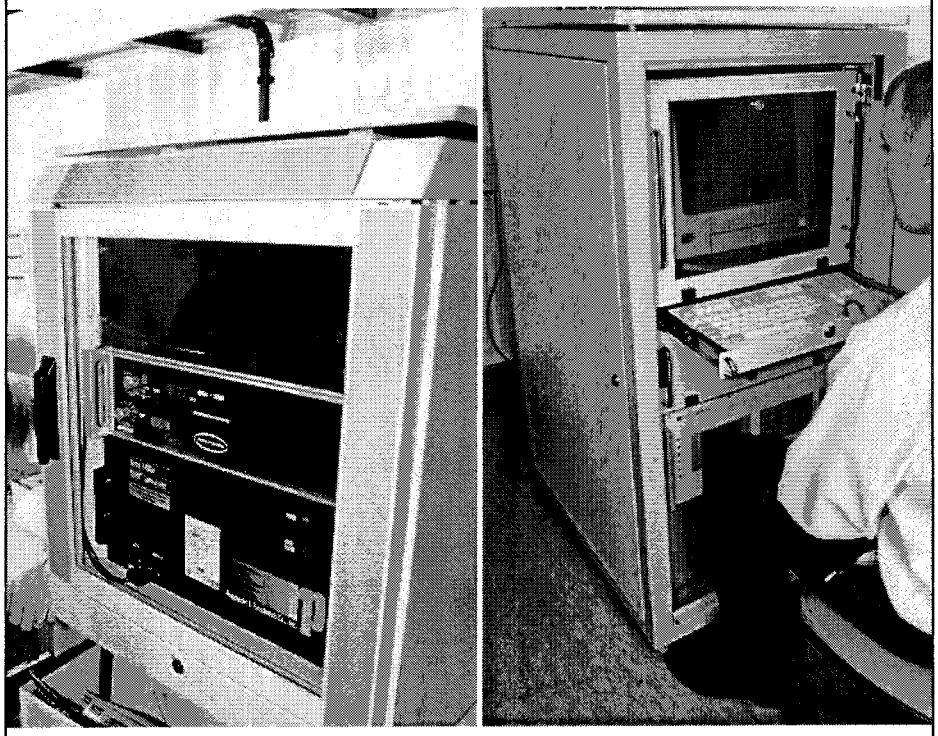
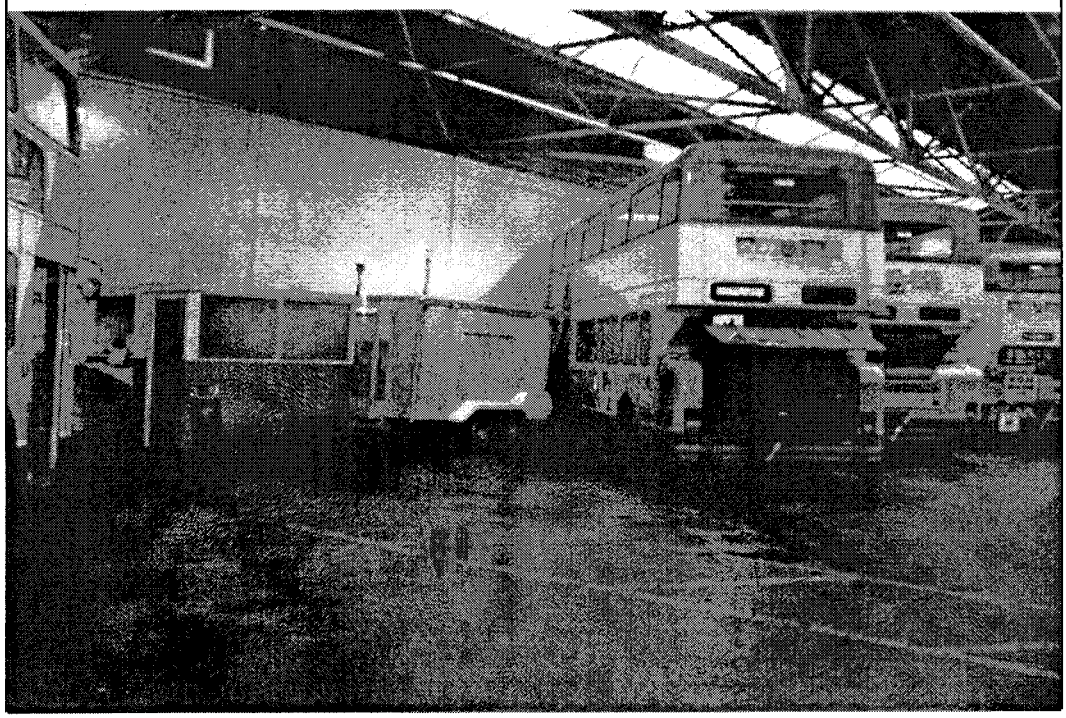


Plate A4.3 Mobile Laboratory Interior



Data Storage Module TD- GC-FID and PC

Plate A4.4 Mobile Laboratory Sampling Location, Bus Depot



APPENDIX 5 SITE CLASSIFICATION

Table A1.1 below presents the classification of site type adopted throughout this document.

Table A5.1 Definition of Site Classes

Class	Description
Kerbside	Sites with sample inlets within 1m of the edge of a busy road. Sampling heights are within 2-3m.
Roadside	Sites with sample inlets between 1m of the kerbside of a busy road and the back of the pavement. Typically this will be within 5m of the kerbside. Sampling heights are within 2-3m.
Urban Centre	Non-kerbside sites located in an area representative of typical population exposure in town or city centre areas e.g. pedestrian precincts and shopping areas. Sampling heights are typically within 2-3m.
Urban Background	Urban locations distanced from sources and broadly representative of city-wide background concentrations e.g. elevated locations, parks and urban residential areas
Urban Industrial	Sites where industrial emissions make an significant contribution to measured pollution levels.
Suburban	Sites typical of residential areas on the outskirts of a town or city.
Suburban Roadside	Sites representative of a town or outskirts of a city typically 5m from the kerbside.
Rural	Open country locations distanced from population centres, roads and industrial areas.
Remote	Open country locations within isolated rural areas, experiencing regional background pollution levels for much of the time.

Adopted from the Department of the Environment, Transport and the Regions (1998)

APPENDIX 6 PUBLICATION

'Analysis of Aromatic Hydrocarbons in Urban Atmospheres'.

Published in the Proceedings of the Trabzon International Energy and Environment Symposium, 1998, Trabzon, Turkey.

Department of Chemical and Life Science,

University of Northumbria, Newcastle upon Tyne

in collaboration with

Department of Public Health and Environmental Protection,
Newcastle upon Tyne

Analysis of Tropospheric Pollutants in Urban Atmospheres

I. James, J. Newham, J. Lee.

Abstract

The number and behavioural diversity of atmospheric Volatile Organic Compounds (VOCs) emitted to the troposphere by road vehicles is far greater than for any other category of pollutant.

Analysis of aromatic hydrocarbons s in North East England has been achieved using an automated thermal desorption - gas chromatography - flame ionisation detector (TD-GC-FID) system. It is mounted in a mobile laboratory, together with a TEOM (Tapered Element Oscillating Microbalance) system for particulate monitoring, and a weather station.

Both systems have been applied to city centre sites in order to examine the pollution loads at these localities and their dependence on traffic flow, surface topography and meteorology. The instrumentation has also been applied to areas of a city center before and after pedestrianisation, the results showing a large reduction in primary traffic pollutants.

INTRODUCTION

The number and behavioural diversity of atmospheric Volatile Organic Compounds (VOC's) is far greater than for any other category of pollutant. Their widespread and growing applications in the petrochemical, plastics, paint, adhesives and textile industries, and the presence of hundreds of VOC's in common fuels and their combustion products, ensures that these compounds will continue to be among the most common atmospheric pollutants.

Their impact on man and his environment is equally diverse. Control efforts currently focus on those substances, which include benzene, 1,3-butadiene and vinyl chloride, that are known carcinogens.[1] Many other VOC's act indirectly, either by producing tropospheric ozone, or via the destruction of stratospheric ozone, or by enhancing global warming.[2] Existing controls are patchy in controlling these problems in a comprehensive manner.

Monitoring and control of VOCs in Newcastle has been directed primarily at major traffic pollutants. Total VOC detectors such as those based on Flame Ionisation Detectors (FID) measurement, and simple devices such as hand pumped detector tubes, can be useful for preliminary screening to

identify source locations, but do not allow identification of the VOC's present.

Continuous monitoring has been achieved with the aid of two major systems. One of these is an open path absorption system, or Differential Optical Absorption Spectroscopy (DOAS) which provides simultaneous 30 minute measurements for formaldehyde, nitrogen monoxide, sulphur dioxide and ozone, along paths approximately 500 m in length at a height of about 100 m above the city centre. The accuracy of this system is dependent on the existence of unique absorption wavelengths for each substance being monitored, in order to avoid interference effects from other pollutants.

The second system used in Newcastle for continuous monitoring is an Automated

Gas Chromatograph (APGC) with an adsorption cartridge for VOC pre-concentration. The unit has been optimised for the measurement of BTEX compounds: benzene, toluene, ethylbenzene, and o-, m- and p-xylenes. It is mounted in a trailer, together with a TEOM (Tapered Element Oscillating Microbalance) system for particulate monitoring, and a weather station.

The trailer is then transported to sites for monitoring over periods of (usually) 2-4 weeks. Calibration of the chromatograph is achieved with the aid of multi-component standard gas mixtures, but a need for multi-point

calibration demands construction of additional sampling facilities.

Both systems have been applied to city centre sites in order to examine the pollution loads at these localities and their dependence on traffic flow, surface topography and meteorology.

The APGC unit has been used to carry out investigations at sites of special interest. The latter have included Sunderland city centre before and after a pedestrianisation scheme (discussed below), Newcastle Airport where the impact of aircraft emissions was of particular interest, and the Tyne -Tunnel, where elevated particulate concentrations coincide with the absence of photochemical removal processes. Comprehensive data analysis for these investigations is in progress.

EVALUATION OF EFFECTS OF PEDESTRIANISATION OF INNER CITY AREAS

Background and Aims

During the period of 1996 - 1997, a pedestrianisation scheme was introduced to the city centre of Sunderland in an attempt to reduce road congestion and improve air quality. The aim of this study was to quantitatively ascertain the change in air quality (whether good or bad) before and after the scheme had been implemented at two locations inside and near to the pedestrianisation area.

The sites chosen for the study were Fawcett Street and Holmeside Street. Fawcett Street, being included in the pedestrianisation, was chosen because it was thought that the biggest reduction in BTEX concentration should be found there. Holmeside Street, however, was not involved in the pedestrianisation, but it was envisaged that the street may convey more traffic because of these changes, and air quality there could deteriorate.

Differential optical absorption spectroscopy (DOAS) was deployed with the path above both streets as shown in the map. In this study, DOAS was used to measure formaldehyde, sulphur dioxide, nitrogen dioxide and ozone. The mobile laboratory was

deployed under the DOAS path, very close to the road of study. In both phases of the study (i.e. before and after pedestrianisation) the equipment was installed to exactly the same location.

INSTRUMENTATION

Thermal Desorption - Gas Chromatography - Flame Ionisation Detector (TD-GC-FID)

TD-GC-FID has been chosen for the analysis of gas phase C_6-C_8 aromatic hydrocarbons. Due to low atmospheric concentration of AH's even in polluted atmospheres, pre-concentration is necessary prior to chromatographic analysis. This was achieved using an adsorbent trap during sampling of the atmospheric gas stream, employing Tenax Gr as the adsorbent material. Tenax Gr is a cross-linked polymer based upon 2,6-diphenylene oxide, with around 20% of its matrix filled with graphite.

The TD-GC-FID system samples the atmosphere for a period of about 15 minutes (user variable) per cycle, passing the sample over a fixed adsorbent bed (Tenax GR) at 40°C to limit retention of lower molecular weight VOC's such as methane.[3] The flow is regulated accurately by means of a mass flow controller. Once sampling is complete, carrier flow (N_2) is directed to flow over the adsorbent and then into a pre-column. The trap is then rapidly heated which causes the organic compounds to desorb and transport to the GC pre-column where the compounds are separated. Flame ionisation detector achieves detection of the separated organic analytes, and the signal produced is integrated using Chrompack PCI software yielding parts per billion by volume (ppbv) values.

Analytical Sequence TD-GC-FID

1 **Sampling** : 15 mins sampling period, organics are adsorbed upon Tenax GR.

2 **Desorption** : The trap is heated to 230°C to release the organic.

3 **Injection** : Desorbed organic sample is transported to the GC pre-column.

4 **Separation** : Pre-column back-flushes higher boiling point compounds.

5 **Detection System** :H_2 / air flame ionisation detection.

: Chrompack CP7001 BTX Monitor.

Differential Optical Absorbance Spectroscopy (DOAS)

DOAS has been found to be most useful for the unattended analysis of part per billion by volume levels of organic and inorganic gas phase pollutants.[4] A light source is placed typically 200-1500 meters from the receiving point. The light crossing this path (the sample atmosphere) is focused by a parabolic mirror in the receiver, the focused light being delivered to the entrance slit of the spectrograph.[4] The grating separates the light into different wavelengths which are projected across the exit slit. A small part of the spectrum is scanned only at one time by means of a slotted disc device, a thin metal disc that has many radially etched slots. The analyser only uses one slot at a time as the exit slit. A photomultiplier tube (PMT) then amplifies the light, and the recorded signals are sent to a computer and stored. By scanning and storing several hundred 'snapshots' of the spectrum at intervals of ~ 0.2 nm, it is possible to reconstruct the absorption spectrum over a region of 20-40 nm. By sequential subtraction, it is possible to determine the spectral absorption contribution of each gaseous analyte.

Results and Interpretation

TD-GC-FID Results

Results yielded by TD-GC-FID in Fawcett Street for Phase I (Jan 1996) and Phase II (Feb 1997) are shown below in tables 1 and 2.

Table 1
KEY [AP= After Pedestrianisation, BP= Before Pedestrianisation]

F BP: **BTEX Concentration at Fawcett Street, During Phase I. Monday 8/1/96 - Wednesday 10/1/96**
F AP: **BTEX Concentration at Fawcett Street, During Phase II. Monday 17/2/97 - Wednesday 19/2/97**
H BP: **BTEX Concentration at Holmeside Street, During Phase I. Thursday 11/1/96 - Friday 12/1/96**
H AP: **BTEX Concentration at Holmeside Street, during Phase II. Thursday 20/2/97 - Friday 21/2/97**

Species (All Data ppbv)	Av.Conc F BP	Av.Conc F AP	Av.Conc H BP	Av.Conc H AP
Benzene	4.6	1.2	2.3	2.1
Toluene	10.9	2.0	5.4	5.5
Ethylbenzene	3.0	1.1	1.5	1.1
Metaxylene	2.3	0.1	1.1	0.9
Paraxylene	4.6	0.1	2.2	1.2
Orthoxylene	3.2	<0.1	1.5	<0.1
Number Samples (n)	47	35	106	46

Table 2 Effect of Pedestrianisation at Fawcett Street.

	Av. Conc. (ppbv) Phase I	Av. Conc. (ppbv) Phase II	% Change after Scheme
Benzene	4.6	1.2	-72.1
Toluene	10.9	2.0	-81.1
Ethylbenzene	3.0	1.1	-61.1
Metaxylene	2.3	0.1	-92.1
Paraxylene	4.6	0.1	-95.9

Table 3 Effect of Pedestrianisation at Holmeside Street

	Av. Conc. (ppbv) Phase I	Av. Conc. (ppbv) Phase II	% Change after Scheme
Benzene	2.3	2.1	-9.1
Toluene	5.4	5.5	+2.0
Ethylbenzene	1.5	1.1	-23.5
Metaxylene	1.1	0.9	-13.2
Paraxylene	1.5	1.2	-21.7

The data has been treated to eliminate variation of the measured concentrations caused by differences in wind speed and direction, by using wind direction as a classifier. For each study phase, periods were selected that contain data collected under conditions of similar wind direction and velocity.

All other sectors were disregarded, and remaining data for the chosen sectors were sorted to determine times where wind speeds were similar ($\pm$ 0.5 ms^{-1}). Changes in concentrations of the BTEX compounds from Phase 1 – Phase 2 during these periods of matched metrology are shown in table below:

Table 4 Effects of Pedestrianisation at Under Conditions of Matched Meteorology

	Fawcett Street (% Change)	Holmeside Street (% Change)
Benzene	-62	-12
Toluene	-65	-1
Ethylbenzene	-63	-23
Metaxylene	-71	-20
Paraxylene	-79	-43

DOAS Results

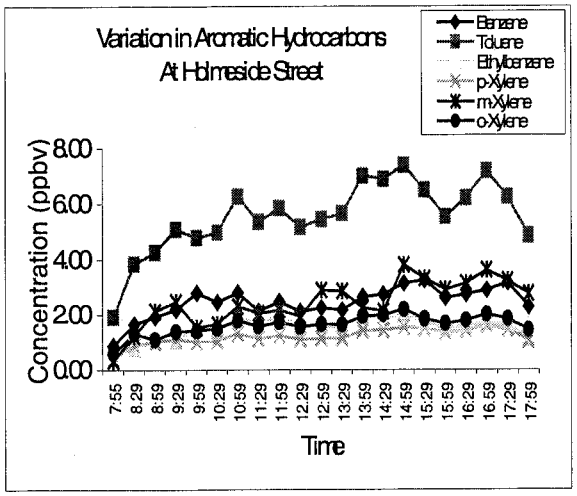
Some of the data has been presented in table 5. There is no strong direct correlation between measurements of the BTEX compounds made at ground level with the species measured by DOAS above the city. There are, however, several interesting findings indicated by the data. Nitrogen dioxide and ozone shown a fair inverse correlation (correl. coef = -0.60, Fawcett Street, phase I). Also, sulphur dioxide does not directly correlate with any of the other pollutants measured, nor does it show a regular diurnal variation. Averages for NO_2, SO_2 and O_3 for both phases are summarised on the table below.

Table 5 DOAS Measurements for Phase I and II

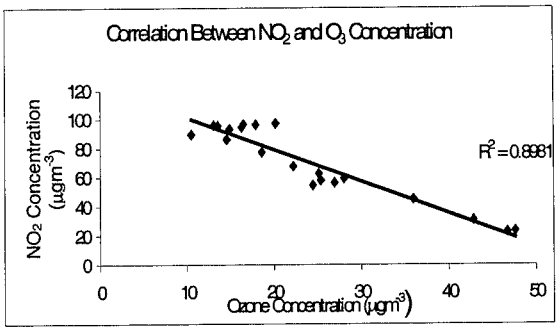
	Ozone (μgm^{-3})	Nitrogen Dioxide (μgm^{-3})	Sulphur Dioxide (μgm^{-3})
Fawcett Street Phase I	27.8	57.7	33.5
Holmeside Street Phase I	32.9	63.2	33.8
Fawcett Street Phase II	63.2	74.9	27.4
Holmeside Street Phase II	49.9	69.7	27.3

CONCLUSION

The untreated data yielded by TD-GC-FID infer that pedestrianisation of Sunderland City centre had decreased the BTEX compound concentration at Fawcett Street significantly, and at Holmeside Street, concentration for all analytes except toluene had reduced. Using wind direction as a classifier, it was shown that during similar periods between study phases,
where wind speeds and directions were comparable, BTEX concentration had reduced considerably at Fawcett Street and slightly at Holmeside Street. In terms of reduction of public exposure to these compounds, pedestrianisation has been successful. All data sets show a common diurnal trend related largely to the intensity of road traffic throughout



the day (see graph 1).



The DOAS system determined that
there was not an observable reduction above
street level in the concentration of ozone, nitrogen dioxide and sulphur dioxide as a result
of the pedestrianisation. Measured ozone and nitrogen dioxide concentrations appeared to be

Graph 1: Diurnal Variation of BTEX Concentration

Graph 2: Correlation Between [NO_2] and [O_3]

site dependent where sulphur dioxide did not.
This could be explained by the fact that should atmospheric conditions prevail that are conducive to poor air mixing, differences in measured NO_2 and O_3 concentrations could exist, both of which are generated in the city centre itself. The measured concentrations of SO_2 are very comparable for the two independent paths. The most likely explanation is that the source is Blyth Power Station, some 20 miles north north east of Sunderland.

The inverse correlation observed between ozone and nitrogen dioxide concentration's is not uncommon (see graph 2).

Vehicle exhaust emissions of NO_x are between 85%-95% nitrogen oxide.[4] NO can be oxidised in the troposphere by the following reaction:

$$NO + O_3 \longrightarrow NO_2 + O_2$$

Hence when the rate of emission of NO is high (e.g. during rush hour), ozone reacts with NO, increasing the concentration of NO_2, and consequently lowering concentrations of ozone. These NO_2 'peaks' usually follow the morning (0730 – 0930hrs) and evening (1600 – 1900hrs) rush hours, and last several hours.

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DATA DISC